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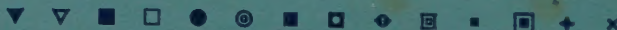
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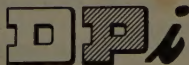
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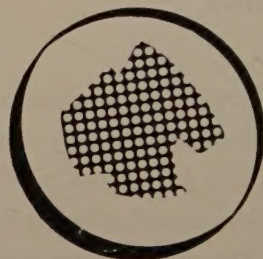
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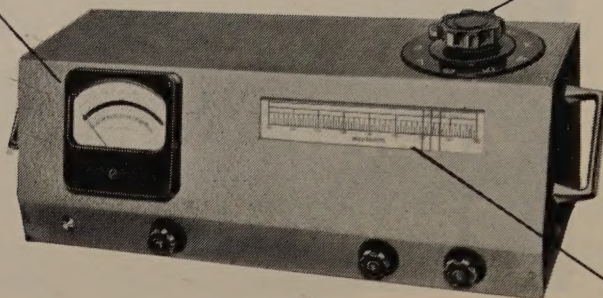
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# SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. II

M. OOSTING

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In a previous paper<sup>1</sup> we derived two expressions for the extraction of a metal ion as a chelate:

$$R^- = \frac{K_{HR}^a \cdot K_w \cdot f \cdot B}{K_w H^+ (f + E_{HR}) + f \{ K_{HR}^b (H^+)^2 + K_{HR}^a K_w \}} \quad (A)$$

and

$$\frac{m^{+n}_{res.}}{a} = \frac{f \cdot L_{MR_n}}{MR_{no\ sat.} (R^-)^n + f \cdot L_{MR_n}} \quad (B)$$

We shall now prove the validity of these expressions and show that they correctly predict the behaviour of metal ions in extraction procedures.

## Calculation of $R^-$

It has proved very helpful to work out the value of  $R^-$  in the form of a table. From equation A we see that the value of  $R^-$  depends on the choice of the system ( $K_{HR}^a$ ,  $K_{HR}^b$ ,  $E_{HR}$ ) and on the conditions used ( $B$ ,  $f$ ,  $H^+$ ).

Initially, only the system oxine – water – chloroform will be considered. Of the conditions,  $f$  is taken as 5, hence only extractions in which the volume of the chloroform phase is one-fifth of that of the aqueous phase will be dealt with.

The relationship between  $B$  and  $R^-$  is linear; accordingly, the  $R^-$ -table is calculated for a value  $B=1$ , and the value of  $R^-$  found in the table need only be multiplied by the actual value of  $B$ . Thus the tabular values of  $R^-$  represent the concentration of oxinate anions in the aqueous phase of a system which contains 1 mg mole of oxine per ml of aqueous phase, and which is in equilibrium with a quantity of chloroform equal to one fifth of the volume of the aqueous phase.

The  $H^+$ -concentration is considered as the auto-variant. The values of  $K_w$ ,  $K_{HR}^a$ ,  $K_{HR}^b$  and  $E_{HR}$  are required. The value of  $K_w$  is well-known; the figure  $1.0 \cdot 10^{-14}$  will be used.

Many data have been published regarding the dissociation constants of oxine. FOX<sup>2</sup> found the value  $K_{HR}^a = 3.68 \cdot 10^{-11}$  from hydrolysis measurements. STONE AND FRIEDMAN<sup>3</sup>, using the solubility method of DAVIDSON<sup>4</sup>, found values between

$4.20 \cdot 10^{-11}$  and  $4.28 \cdot 10^{-11}$ . PHILIPS AND MERRIT<sup>5</sup>, using the optical method of STENSTROM AND GOLDSMITH<sup>6</sup>, found  $pK_{\text{HR}}^a = 9.70$  ( $K_{\text{HR}}^a = 1.95 \cdot 10^{-10}$ ) and  $pK_{\text{HR}}^b = 9.08$  ( $K_{\text{HR}}^b = 8.32 \cdot 10^{-10}$ ). From potentiometric titrations BORREL AND PÂRIS<sup>7</sup> found  $pK_{\text{HR}}^a = 9.85$  and  $p''K_{\text{HR}}^b = 5.05$ . This " $K_{\text{HR}}^b$ " is not the same as "our"  $K_{\text{HR}}^b$ , but is related to it by the simple equation:  $K_{\text{HR}}^b$  (our definition) =  $K_w / K_{\text{HR}}^b$ , and accordingly  $pK_{\text{HR}}^b = 8.95$ . BOCQUET AND PÂRIS<sup>8</sup>, comparing potentiometric and optical methods, found  $pK_{\text{HR}}^a = 9.82$  and  $p''K_{\text{HR}}^b = 5.10$ . In good agreement are also the values  $pK_{\text{HR}}^a = 9.82$  and  $pK_{\text{HR}}^b = 5.09$  found by LACROIX<sup>9</sup>. UMLAND AND PUCHELT<sup>10</sup> found  $pK_{\text{HR}}^a = 9.60$  and  $p''K_{\text{HR}}^b = 5.33$ , by extracting oxine with benzene at various pH-values. These values are based on the determination of the partition coefficient and therefore are as inaccurate as the bromatometric determination of 11  $\mu\text{g}$  of oxine in 50 ml of aqueous solution.

The values  $K_{\text{HR}}^a = 1.3 \cdot 10^{-10}$  and  $K_{\text{HR}}^b = 1.2 \cdot 10^{-9}$ , will be used here; these are based on earlier work<sup>7-9</sup>.

For the partition coefficient of oxine between water and chloroform values of 720<sup>9</sup> and 350<sup>11</sup> have been given. These values disagree, hence the determination of the value of  $E_{\text{HR}}$  was repeated.

A quantity of oxine was weighed exactly and shaken for 20 h with chloroform and an aqueous buffer solution. The volumes of both phases were determined. In the aqueous phase the pH was measured and the sum of undissociated oxine and oxinate ion was determined by bromatometric titration.

With the known value of  $K_{\text{HR}}^a$ , the concentration of undissociated oxine was calculated. The term  $K_{\text{HR}}^b$  was neglected, which is allowed at the pH values considered.

The quantity of oxine in the chloroform phase was obtained from the difference between the amount of oxine taken and the amount of oxine + oxinate found in the aqueous phase.

In the first experiment, 346.2 mg of oxine (2.387 mg moles) were shaken in a glass-stoppered measuring cylinder with aqueous buffer and chloroform and the layers were allowed to separate; the volumes of aqueous and chloroform phases were 33.5 and 25 ml respectively.

The pH of the aqueous phase, measured with a glass electrode, was 8.71, thus  $\text{H}^+ = 2 \cdot 10^{-9}$ .

To 20 ml of the aqueous phase 3.18 ml of 0.1004 *N* bromate solution, 250 mg of potassium bromide and 5 ml of 6 *N* HCl were added. The excess of bromate was back-titrated with 2.81 ml of 0.1000 *N* thiosulphate.

The aqueous phase thus contained 0.0644 mg equivs. or 0.0161 mg moles of oxine + oxinate.

$$\text{Ox}^- + \text{HOx} = 0.0161 \quad \dots \quad (1)$$

$$K_{\text{HR}}^a = \frac{\text{H}^+ \cdot \text{Ox}^-}{\text{HOx}} = 1.3 \cdot 10^{-10},$$

$$2.10^{-9} \cdot \text{Ox}^- = 1.3 \cdot 10^{-10} \text{ HOx}$$

$$\text{or } \text{Ox}^- = 0.065 \text{ HOx} \quad \dots \quad (2)$$

TABLE I

$pH$	$R^-$	$(R^-)^2$	$(R^-)^3$	$pH$	$R^-$	$(R^-)^2$	$(R^-)^3$
1.0	$1.1 \cdot 10^{-13}$	$1.2 \cdot 10^{-26}$	$1.3 \cdot 10^{-39}$	4.0	$2.4 \cdot 10^{-8}$	$5.8 \cdot 10^{-16}$	$1.4 \cdot 10^{-23}$
1.1	$1.7 \cdot 10^{-13}$	$2.9 \cdot 10^{-26}$	$4.9 \cdot 10^{-39}$	4.1	$3.1 \cdot 10^{-8}$	$9.6 \cdot 10^{-16}$	$3.0 \cdot 10^{-23}$
1.2	$2.7 \cdot 10^{-13}$	$7.3 \cdot 10^{-26}$	$2.0 \cdot 10^{-38}$	4.2	$4.3 \cdot 10^{-8}$	$1.8 \cdot 10^{-15}$	$8.0 \cdot 10^{-23}$
1.3	$4.3 \cdot 10^{-13}$	$1.8 \cdot 10^{-25}$	$8.0 \cdot 10^{-38}$	4.3	$5.0 \cdot 10^{-8}$	$2.5 \cdot 10^{-15}$	$1.3 \cdot 10^{-22}$
1.4	$6.5 \cdot 10^{-13}$	$4.2 \cdot 10^{-25}$	$2.7 \cdot 10^{-37}$	4.4	$6.9 \cdot 10^{-8}$	$4.8 \cdot 10^{-15}$	$3.3 \cdot 10^{-22}$
1.5	$1.1 \cdot 10^{-12}$	$1.2 \cdot 10^{-24}$	$1.3 \cdot 10^{-36}$	4.5	$9.0 \cdot 10^{-8}$	$8.1 \cdot 10^{-15}$	$7.3 \cdot 10^{-22}$
1.6	$1.7 \cdot 10^{-12}$	$2.9 \cdot 10^{-24}$	$4.9 \cdot 10^{-36}$	4.6	$1.1 \cdot 10^{-7}$	$1.2 \cdot 10^{-14}$	$1.3 \cdot 10^{-21}$
1.7	$2.7 \cdot 10^{-12}$	$7.3 \cdot 10^{-24}$	$2.0 \cdot 10^{-35}$	4.7	$1.5 \cdot 10^{-7}$	$2.3 \cdot 10^{-14}$	$3.4 \cdot 10^{-21}$
1.8	$4.1 \cdot 10^{-12}$	$1.7 \cdot 10^{-23}$	$6.9 \cdot 10^{-35}$	4.8	$1.9 \cdot 10^{-7}$	$3.6 \cdot 10^{-14}$	$6.9 \cdot 10^{-21}$
1.9	$6.5 \cdot 10^{-12}$	$4.2 \cdot 10^{-23}$	$2.7 \cdot 10^{-34}$	4.9	$2.4 \cdot 10^{-7}$	$5.8 \cdot 10^{-14}$	$1.4 \cdot 10^{-20}$
2.0	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-22}$	$1.0 \cdot 10^{-33}$	5.0	$3.0 \cdot 10^{-7}$	$9.0 \cdot 10^{-14}$	$2.7 \cdot 10^{-20}$
2.1	$1.6 \cdot 10^{-11}$	$2.6 \cdot 10^{-22}$	$4.1 \cdot 10^{-33}$	5.1	$3.8 \cdot 10^{-7}$	$1.4 \cdot 10^{-13}$	$5.5 \cdot 10^{-20}$
2.2	$2.6 \cdot 10^{-11}$	$6.8 \cdot 10^{-22}$	$1.8 \cdot 10^{-32}$	5.2	$5.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-13}$	$1.3 \cdot 10^{-19}$
2.3	$4.1 \cdot 10^{-11}$	$1.7 \cdot 10^{-21}$	$6.9 \cdot 10^{-32}$	5.3	$6.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-13}$	$2.2 \cdot 10^{-19}$
2.4	$5.9 \cdot 10^{-11}$	$3.5 \cdot 10^{-21}$	$2.1 \cdot 10^{-31}$	5.4	$7.6 \cdot 10^{-7}$	$5.8 \cdot 10^{-13}$	$4.4 \cdot 10^{-19}$
2.5	$9.8 \cdot 10^{-11}$	$9.6 \cdot 10^{-21}$	$9.4 \cdot 10^{-31}$	5.5	$9.7 \cdot 10^{-7}$	$9.4 \cdot 10^{-13}$	$9.1 \cdot 10^{-19}$
2.6	$1.5 \cdot 10^{-10}$	$2.3 \cdot 10^{-20}$	$3.4 \cdot 10^{-30}$	5.6	$1.2 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$	$1.7 \cdot 10^{-18}$
2.7	$2.3 \cdot 10^{-10}$	$5.3 \cdot 10^{-20}$	$1.2 \cdot 10^{-29}$	5.7	$1.5 \cdot 10^{-6}$	$2.3 \cdot 10^{-12}$	$3.4 \cdot 10^{-18}$
2.8	$3.4 \cdot 10^{-10}$	$1.2 \cdot 10^{-19}$	$3.9 \cdot 10^{-29}$	5.8	$2.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-12}$	$8.0 \cdot 10^{-18}$
2.9	$5.0 \cdot 10^{-10}$	$2.5 \cdot 10^{-19}$	$1.3 \cdot 10^{-28}$	5.9	$2.5 \cdot 10^{-6}$	$6.3 \cdot 10^{-12}$	$1.6 \cdot 10^{-17}$
3.0	$8.0 \cdot 10^{-10}$	$6.4 \cdot 10^{-19}$	$5.1 \cdot 10^{-28}$	6.0	$3.1 \cdot 10^{-6}$	$9.6 \cdot 10^{-12}$	$3.0 \cdot 10^{-17}$
3.1	$1.2 \cdot 10^{-9}$	$1.4 \cdot 10^{-18}$	$1.7 \cdot 10^{-27}$	6.1	$3.8 \cdot 10^{-6}$	$1.4 \cdot 10^{-11}$	$5.5 \cdot 10^{-17}$
3.2	$1.8 \cdot 10^{-9}$	$3.2 \cdot 10^{-18}$	$5.8 \cdot 10^{-27}$	6.2	$5.0 \cdot 10^{-6}$	$2.5 \cdot 10^{-11}$	$1.3 \cdot 10^{-16}$
3.3	$2.5 \cdot 10^{-9}$	$6.3 \cdot 10^{-18}$	$1.6 \cdot 10^{-26}$	6.3	$6.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-11}$	$2.2 \cdot 10^{-16}$
3.4	$3.6 \cdot 10^{-9}$	$1.3 \cdot 10^{-17}$	$4.7 \cdot 10^{-26}$	6.4	$7.7 \cdot 10^{-6}$	$5.9 \cdot 10^{-11}$	$4.6 \cdot 10^{-16}$
3.5	$5.0 \cdot 10^{-9}$	$2.5 \cdot 10^{-17}$	$1.3 \cdot 10^{-25}$	6.5	$9.8 \cdot 10^{-6}$	$9.6 \cdot 10^{-11}$	$9.4 \cdot 10^{-16}$
3.6	$7.1 \cdot 10^{-9}$	$5.0 \cdot 10^{-17}$	$3.6 \cdot 10^{-25}$	6.6	$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-10}$	$1.7 \cdot 10^{-15}$
3.7	$9.8 \cdot 10^{-9}$	$9.6 \cdot 10^{-17}$	$9.4 \cdot 10^{-25}$	6.7	$1.5 \cdot 10^{-5}$	$2.3 \cdot 10^{-10}$	$3.4 \cdot 10^{-15}$
3.8	$1.3 \cdot 10^{-8}$	$1.7 \cdot 10^{-16}$	$2.2 \cdot 10^{-24}$	6.8	$2.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-10}$	$8.0 \cdot 10^{-15}$
3.9	$1.8 \cdot 10^{-8}$	$3.2 \cdot 10^{-16}$	$5.8 \cdot 10^{-24}$	6.9	$2.5 \cdot 10^{-5}$	$6.3 \cdot 10^{-10}$	$1.6 \cdot 10^{-14}$

TABLE I (continued)

$pH$	$R^-$	$(R^-)^2$	$(R^-)^3$	$pH$	$R^-$	$(R^-)^2$	$(R^-)^3$
7.0	$3.1 \cdot 10^{-5}$	$9.6 \cdot 10^{-10}$	$3.0 \cdot 10^{-14}$	10.0	$3.0 \cdot 10^{-2}$	$9.0 \cdot 10^{-4}$	$2.7 \cdot 10^{-5}$
7.1	$3.8 \cdot 10^{-5}$	$1.4 \cdot 10^{-9}$	$5.5 \cdot 10^{-14}$	10.1	$3.6 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$	$4.7 \cdot 10^{-5}$
7.2	$5.0 \cdot 10^{-5}$	$2.5 \cdot 10^{-9}$	$1.3 \cdot 10^{-13}$	10.2	$4.6 \cdot 10^{-2}$	$2.1 \cdot 10^{-3}$	$9.7 \cdot 10^{-5}$
7.3	$6.0 \cdot 10^{-5}$	$3.6 \cdot 10^{-9}$	$2.2 \cdot 10^{-13}$	10.3	$5.4 \cdot 10^{-2}$	$2.9 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$
7.4	$7.7 \cdot 10^{-5}$	$5.9 \cdot 10^{-9}$	$4.6 \cdot 10^{-13}$	10.4	$7.1 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$
7.5	$9.8 \cdot 10^{-5}$	$9.6 \cdot 10^{-9}$	$4.9 \cdot 10^{-13}$	10.5	$8.9 \cdot 10^{-2}$	$7.9 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$
7.6	$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-8}$	$1.7 \cdot 10^{-12}$	10.6	$1.1 \cdot 10^{-1}$	$1.2 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$
7.7	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{-8}$	$3.4 \cdot 10^{-12}$	10.7	$1.3 \cdot 10^{-1}$	$1.7 \cdot 10^{-2}$	$2.2 \cdot 10^{-3}$
7.8	$2.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-8}$	$8.0 \cdot 10^{-12}$	10.8	$1.6 \cdot 10^{-1}$	$2.6 \cdot 10^{-2}$	$4.1 \cdot 10^{-3}$
7.9	$2.5 \cdot 10^{-4}$	$6.3 \cdot 10^{-8}$	$1.6 \cdot 10^{-11}$	10.9	$2.0 \cdot 10^{-1}$	$4.0 \cdot 10^{-2}$	$8.0 \cdot 10^{-3}$
8.0	$3.1 \cdot 10^{-4}$	$9.6 \cdot 10^{-8}$	$3.0 \cdot 10^{-11}$	11.0	$2.3 \cdot 10^{-1}$	$5.3 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
8.1	$3.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-7}$	$5.5 \cdot 10^{-11}$	11.1	$2.7 \cdot 10^{-1}$	$7.3 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
8.2	$5.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-7}$	$1.3 \cdot 10^{-10}$	11.2	$3.3 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$3.6 \cdot 10^{-2}$
8.3	$6.0 \cdot 10^{-4}$	$3.6 \cdot 10^{-7}$	$2.2 \cdot 10^{-10}$	11.3	$3.6 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	$4.7 \cdot 10^{-2}$
8.4	$7.7 \cdot 10^{-4}$	$5.9 \cdot 10^{-7}$	$4.6 \cdot 10^{-10}$	11.4	$4.3 \cdot 10^{-1}$	$1.8 \cdot 10^{-1}$	$8.0 \cdot 10^{-2}$
8.5	$9.8 \cdot 10^{-4}$	$9.6 \cdot 10^{-7}$	$9.4 \cdot 10^{-10}$	11.5	$5.0 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$
8.6	$1.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-6}$	$1.7 \cdot 10^{-9}$	11.6	$5.4 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$
8.7	$1.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-9}$	11.7	$5.9 \cdot 10^{-1}$	$3.5 \cdot 10^{-1}$	$2.1 \cdot 10^{-1}$
8.8	$2.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-6}$	$8.0 \cdot 10^{-9}$	11.8	$6.6 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$
8.9	$2.5 \cdot 10^{-3}$	$6.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-8}$	11.9	$7.1 \cdot 10^{-1}$	$5.0 \cdot 10^{-1}$	$3.6 \cdot 10^{-1}$
9.0	$3.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-6}$	$3.0 \cdot 10^{-8}$	12.0	$7.6 \cdot 10^{-1}$	$5.8 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$
9.1	$3.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-5}$	$5.5 \cdot 10^{-8}$	12.1	$7.9 \cdot 10^{-1}$	$6.2 \cdot 10^{-1}$	$4.9 \cdot 10^{-1}$
9.2	$5.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-5}$	$1.3 \cdot 10^{-7}$	12.2	$8.3 \cdot 10^{-1}$	$6.9 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$
9.3	$6.0 \cdot 10^{-3}$	$3.6 \cdot 10^{-5}$	$2.2 \cdot 10^{-7}$	12.3	$8.6 \cdot 10^{-1}$	$7.4 \cdot 10^{-1}$	$6.4 \cdot 10^{-1}$
9.4	$7.6 \cdot 10^{-3}$	$5.8 \cdot 10^{-5}$	$4.4 \cdot 10^{-7}$	12.4	$8.9 \cdot 10^{-1}$	$7.9 \cdot 10^{-1}$	$7.0 \cdot 10^{-1}$
9.5	$9.7 \cdot 10^{-3}$	$9.4 \cdot 10^{-5}$	$9.1 \cdot 10^{-7}$	12.5	$9.0 \cdot 10^{-1}$	$8.1 \cdot 10^{-1}$	$7.3 \cdot 10^{-1}$
9.6	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-6}$	12.6	$9.3 \cdot 10^{-1}$	$8.6 \cdot 10^{-1}$	$8.0 \cdot 10^{-1}$
9.7	$1.5 \cdot 10^{-2}$	$2.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	12.7	$9.4 \cdot 10^{-1}$	$8.8 \cdot 10^{-1}$	$8.3 \cdot 10^{-1}$
9.8	$1.9 \cdot 10^{-2}$	$3.6 \cdot 10^{-4}$	$6.9 \cdot 10^{-6}$	12.8	$9.6 \cdot 10^{-1}$	$9.2 \cdot 10^{-1}$	$8.8 \cdot 10^{-1}$
9.9	$2.4 \cdot 10^{-2}$	$5.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$	12.9	$9.6 \cdot 10^{-1}$	$9.3 \cdot 10^{-1}$	$9.0 \cdot 10^{-1}$
				13.0	$9.7 \cdot 10^{-1}$	$9.4 \cdot 10^{-1}$	$9.1 \cdot 10^{-1}$

From (1) and (2),

$$1.065 \text{ HOx} = 0.0161 \text{ or HOx} = 0.0151 \text{ mg moles.}$$

and the concentration is therefore 0.00045 mg mole/ml.

The chloroform phase contained  $2.387 - 0.016 = 2.371$  mg moles of oxine and so its concentration was 0.0948 mg moles/ml.

From these data,

$$E = \frac{\text{concn. HOx in chloroform}}{\text{concn. HOx in water}} = \frac{0.0948}{0.00045} = 211.$$

When the experiment was repeated, the values  $E = 210$  and  $E = 194$  were found at pH 9.04 and 9.62 respectively.

In the following calculations the mean value  $E = 205$  is used. It is not clear why three investigators have found such divergent values.

The results of the calculations of  $R^-$  as a function of  $H^+$  are given in Table I. As this has proved to be useful when dealing with bi- and trivalent metal ions, the values of  $(R^-)^2$  and  $(R^-)^3$  are also included.

#### Checking of the equations

To check the validity of our equations and the suppositions on which they are based, we have used the extractions of copper and nickel with oxine and chloroform.

#### Copper-oxine-chloroform

For the expression

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL_{MR_n}}{MR_{no} \text{ sat. } (R^-)^n + fL_{MR_n}}$$

the values of  $L_{MR_n}$  and  $MR_{no} \text{ sat.}$  are still required.

The value of  $L_{MR_n}$  is given by BORREL AND PÂRIS<sup>7</sup> as  $5 \cdot 10^{-29}$ . The value of  $7.4 \cdot 10^{-10}$  found by TREADWELL AND AMMAN<sup>12</sup> is incorrect. This value was calculated from the solubility of copper oxinate in 1 N acetic acid without considering the amphoteric character of oxine; accordingly, it is too large.

The value of  $\text{CuOx}_2 \text{ sat. chloroform}$  was determined by shaking chloroform for 24 h with pure copper oxinate, distilling the chloroform, destroying the organic matter with sulphuric-perchloric acids in the presence of ammonium vanadate<sup>14</sup>, and by final gravimetric determination of copper.

The value  $3.4 \cdot 10^{-3}$  mg moles/ml was found.

#### The experimental extraction error

In a separatory funnel were placed 49 ml of water\*, 1 ml of a copper sulphate solution containing 1 mg Cu/ml, 1 ml of chloroform containing 56.2 mg of oxine/ml, 9 ml of chloroform\* and a few drops of 2 N hydrochloric acid. The stoppered funnel was shaken for  $5 \times 2$  min, with 2 min between each shaking period. After final

\* In order to avoid large changes of volume of the phases, the water and the chloroform used were saturated with chloroform and water respectively.

separation of the layers, the pH of the aqueous layer was determined as well as the copper content of the chloroform layer and in some cases, the copper content of the aqueous layer.

Copper was determined in the chloroform layer by measuring the absorbance at 450  $m\mu$ . A standard curve was prepared by dissolving a weighed amount of pure copper oxinate in chloroform and measuring the absorbance at 450  $m\mu$  of known dilutions of this solution.

Copper was determined in the aqueous layer with rubeanic acid<sup>13</sup> after destruction of organic matter with sulphuric-perchloric acids in the presence of ammonium vanadate<sup>14</sup>. The results are given in Table II.

TABLE II

pH	aqueous phase	chloroform phase	
	mg of copper rubeanic acid	mg of copper	
		as oxinate	rubeanic acid
1.64		< 0.01	
1.96		0.04	
2.10		0.19	
2.12		0.14	
2.20		0.26	0.28
2.25	0.61	0.37	
2.36	0.36	0.64	0.68
2.50	0.21		0.86
2.55	0.09		
2.85	< 0.01		
3.04	< 0.01		

#### The calculated extraction error

In our experiments the value of  $B$  (defined as  $b/V_w$ ) was  $56.2/145 \cdot 1/50 = 8 \cdot 10^{-3}$ , hence the values of  $(R^-)^2$  found in Table I must be multiplied by  $B^2 = 6.4 \cdot 10^{-5}$ . Only

TABLE III

pH	$(R^-)_{B=1}^2$	$(R^-)_{B=8 \cdot 10^{-3}}^2$	$\text{CuOx}_2 \text{ sat. } (R^-)^2$	$f \text{ Lcux}_2$	$\frac{m^{1/2} \text{ res.}}{a}$
1.6	$2.9 \cdot 10^{-24}$	$1.8 \cdot 10^{-28}$	$6.1 \cdot 10^{-31}$	$2.5 \cdot 10^{-28}$	1.00
1.7	$7.3 \cdot 10^{-24}$	$4.7 \cdot 10^{-28}$	$1.6 \cdot 10^{-30}$		1.00
1.8	$1.7 \cdot 10^{-23}$	$1.1 \cdot 10^{-27}$	$3.7 \cdot 10^{-30}$		1.00
1.9	$4.2 \cdot 10^{-23}$	$2.7 \cdot 10^{-27}$	$9.2 \cdot 10^{-30}$		0.96
2.0	$1.0 \cdot 10^{-22}$	$6.4 \cdot 10^{-27}$	$2.2 \cdot 10^{-29}$		0.93
2.1	$2.6 \cdot 10^{-22}$	$1.7 \cdot 10^{-26}$	$5.8 \cdot 10^{-29}$		0.81
2.2	$6.8 \cdot 10^{-22}$	$4.4 \cdot 10^{-26}$	$1.5 \cdot 10^{-28}$		0.63
2.3	$1.7 \cdot 10^{-21}$	$1.1 \cdot 10^{-25}$	$3.7 \cdot 10^{-28}$		0.40
2.4	$3.5 \cdot 10^{-21}$	$2.2 \cdot 10^{-25}$	$7.5 \cdot 10^{-28}$		0.25
2.5	$9.6 \cdot 10^{-21}$	$6.1 \cdot 10^{-25}$	$2.1 \cdot 10^{-27}$		0.11
2.6	$2.3 \cdot 10^{-20}$	$1.5 \cdot 10^{-24}$	$5.1 \cdot 10^{-27}$		0.04
2.7	$5.3 \cdot 10^{-20}$	$3.4 \cdot 10^{-24}$	$1.2 \cdot 10^{-26}$		0.02
2.8	$1.2 \cdot 10^{-19}$	$7.7 \cdot 10^{-24}$	$2.6 \cdot 10^{-26}$		0.01
2.9	$2.5 \cdot 10^{-19}$	$1.6 \cdot 10^{-23}$	$5.4 \cdot 10^{-26}$		0.005
3.0	$6.4 \cdot 10^{-19}$	$4.1 \cdot 10^{-23}$	$1.4 \cdot 10^{-25}$		0.002

the pH range of 1.6 to 3.0 will be considered. From the values of  $(R^-)^2$  obtained, the values of

$$\frac{m^{+2}\text{res.}}{a} = \frac{fL_{MR_2}}{MR_2 \text{ o sat. } (R^-)^2 + fL_{MR_2}}$$

can be calculated (Table III).

The experimental and the calculated values are shown in Fig. 1, curve I.

The experiments were repeated with a smaller amount of oxine ( $B = 4.3 \cdot 10^{-3}$ ).

The results as well as the calculated values are shown in Fig. 1, curve II.

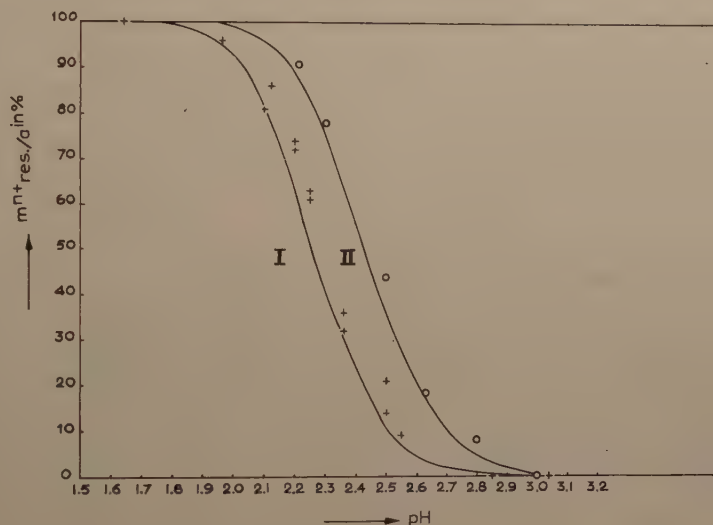


Fig. 1. The extraction of copper with oxine and chloroform as a function of pH. Curve I. Calculated extraction error  $B = 8 \cdot 10^{-3}$ . + = experimentally found extraction error. Curve II. Calculated extraction error  $B = 4.3 \cdot 10^{-3}$ . o = experimentally found extraction error.

### Nickel-oxine-chloroform

The values of  $f$ ,  $B$ ,  $A$  and  $n$ , which depend only on the conditions chosen can be calculated in the same way as in the experiments with copper-oxine-chloroform. The values of  $K_w$ ,  $K_{HR}^a$ ,  $K_{HR}^b$  and  $E_{HR}$  are also the same, of course.

For the solubility product of nickel oxinate, IRVING AND WILLIAMS<sup>15</sup> found a value of  $7.9 \cdot 10^{-23}$ . From the experimental data of BORREL AND PÂRIS<sup>7</sup>, a value of  $7 \cdot 10^{-23}$  can be calculated, and this is used in the following calculations.

The solubility of nickel oxinate in chloroform was determined by shaking pure nickel oxinate for 24 h and determining the nickel in the solution. This solubility proved to be nil, hence it would seem that no extraction is possible. Nevertheless, this extraction has been published<sup>15-18</sup>. Surprisingly, when a nickel solution (pH = 6) is shaken with a solution of oxine in chloroform a definite extraction is obtained. The chloroform solutions, however, are very unstable, nickel oxinate precipitates and after a short time the chloroform is free of nickel.

It can be assumed that the undissociated but not yet precipitated nickel oxinate is extracted from the aqueous phase, and forms chloroform-insoluble  $\text{NiOx}_2 \cdot 2 \text{ aq}$  with the water dissolved in the chloroform. UMLAND AND HOFFMANN<sup>19</sup> found that chloroform solutions of metal oxinates were stabilized by the addition of polar organic compounds, *n*-butylamine being one of the most effective. It is supposed that the *n*-butylamine replaces the water in an equilibrium:



in which b.a. is written for *n*-butylamine. The compound  $\text{NiOx}_2 \cdot 2 \text{ b.a.}$  is soluble in chloroform.

The solubility of nickel oxinate was therefore determined in chloroform in presence of *n*-butylamine by shaking an aqueous solution of nickel sulphate containing a large excess of *n*-butylamine with a chloroform solution of oxine for 8 h. At the end of this period, the aqueous phase contained a green precipitate of nickel oxinate which proved to be readily soluble in chloroform, therefore the chloroform phase was considered to be a saturated solution of nickel oxinate\*. The concentration of nickel oxinate in this perfectly stable solution was found to be  $5.0 \cdot 10^{-2}$  mg moles/ml.

#### *The experimental extraction error*

50 ml of water containing 1 mg of nickel as nickel sulphate, 1 ml of *n*-butylamine and a few drops of dilute sulphuric acid were shaken with a solution of 49.5 mg of oxine in 10 ml of chloroform. After separation of the phases, the pH of the aqueous phase was measured; in the aqueous and/or chloroform phase, nickel was determined colorimetrically with dimethylglyoxime<sup>20</sup> after the destruction of oxine with sulphuric-perchloric acids.

The results are given in Table IV.

TABLE IV

pH	aqueous phase mg of nickel	chloroform phase mg of nickel
2.91	1.00	0.02
3.10	0.96	0.03
3.16		0.10
3.40	0.56	
3.60	0.25	0.74
3.79	0.09	
4.03	0.03	
4.66	0.00	1.00
6.47	0.00	1.02

#### *The calculated extraction error*

From the values  $L_{\text{NiOx}_2} = 7 \cdot 10^{-23}$ ,  $\text{NiOx}_2 \text{ sat. chloroform} = 5 \cdot 10^{-2}$ , R- from Table I, using  $B = 49.5/145 \cdot 1/50 = 6.8 \cdot 10^{-3}$ , the extraction error can be calculated.

The calculations are shown in Table V.

\* We consider the reaction:  $\text{NiOx}_2 + 2 \text{ b.a.} \rightarrow \text{NiOx}_2 \cdot 2 \text{ b.a.}$  a secondary one, which is of no importance for our purposes.

TABLE V

<i>pH</i>	$(R^-)_{B=1}^2$	$(R^-)_{B=0.8 \cdot 10^{-2}}^2$	$NiOx_{\Sigma} sat. (R^-)_{\Sigma}$	$f L_{NiOx_{\Sigma}}$	$\frac{m^{+2} res.}{a}$
2.7	$5.3 \cdot 10^{-20}$	$2.5 \cdot 10^{-24}$	$1.2 \cdot 10^{-25}$	$3.5 \cdot 10^{-23}$	1.00
2.8	$1.2 \cdot 10^{-19}$	$5.6 \cdot 10^{-24}$	$2.8 \cdot 10^{-25}$		0.99
2.9	$2.5 \cdot 10^{-19}$	$1.2 \cdot 10^{-23}$	$5.8 \cdot 10^{-25}$		0.98
3.0	$6.4 \cdot 10^{-19}$	$3.0 \cdot 10^{-23}$	$1.5 \cdot 10^{-24}$		0.96
3.1	$1.4 \cdot 10^{-18}$	$6.6 \cdot 10^{-23}$	$3.3 \cdot 10^{-24}$		0.91
3.2	$3.2 \cdot 10^{-18}$	$1.5 \cdot 10^{-22}$	$7.5 \cdot 10^{-24}$		0.82
3.3	$6.3 \cdot 10^{-18}$	$3.0 \cdot 10^{-22}$	$1.5 \cdot 10^{-23}$		0.70
3.4	$1.3 \cdot 10^{-17}$	$6.1 \cdot 10^{-22}$	$3.0 \cdot 10^{-23}$		0.54
3.5	$2.5 \cdot 10^{-17}$	$1.2 \cdot 10^{-21}$	$5.8 \cdot 10^{-23}$		0.38
3.6	$5.0 \cdot 10^{-17}$	$2.4 \cdot 10^{-21}$	$1.2 \cdot 10^{-22}$		0.23
3.7	$9.6 \cdot 10^{-17}$	$4.5 \cdot 10^{-21}$	$2.2 \cdot 10^{-22}$		0.14
3.8	$1.7 \cdot 10^{-16}$	$8.0 \cdot 10^{-21}$	$4.0 \cdot 10^{-22}$		0.08
3.9	$3.2 \cdot 10^{-16}$	$1.5 \cdot 10^{-20}$	$7.5 \cdot 10^{-22}$		0.04
4.0	$5.8 \cdot 10^{-16}$	$2.7 \cdot 10^{-20}$	$1.4 \cdot 10^{-21}$		0.02
4.1	$9.6 \cdot 10^{-16}$	$4.5 \cdot 10^{-20}$	$2.2 \cdot 10^{-21}$		0.02
4.2	$1.8 \cdot 10^{-15}$	$8.5 \cdot 10^{-20}$	$4.2 \cdot 10^{-21}$		0.01
4.3	$2.5 \cdot 10^{-15}$	$1.2 \cdot 10^{-19}$	$5.8 \cdot 10^{-21}$		0.01
4.4	$4.8 \cdot 10^{-15}$	$2.3 \cdot 10^{-19}$	$1.1 \cdot 10^{-20}$		0.00
4.5	$8.1 \cdot 10^{-15}$	$3.8 \cdot 10^{-19}$	$1.9 \cdot 10^{-20}$		0.00

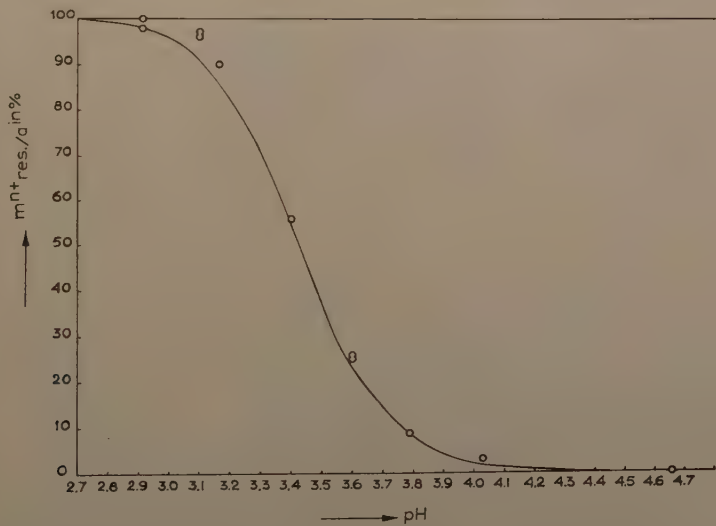


Fig. 2. The extraction of nickel with oxine and chloroform in presence of *n*-butylamine as a function of pH. Calculated and experimentally found extraction errors.

The calculated values and the experimentally found extraction errors are shown in Fig. 2.

It can be concluded that in both systems the course of the extraction is predicted correctly by the equations given in our previous paper<sup>1</sup>.

## SUMMARY

The equations given in a previous paper are shown to predict the course of solvent extraction correctly in the case of copper - oxine - chloroform as well as that of nickel - oxine - chloroform. Both pH and quantity of reagent prove to have the effect required by the equations.

## RÉSUMÉ

Les équations proposées dans le premier article de cette série ont été appliquées aux cas suivants d'extraction par solvant: cuivre-oxine-chloroforme et nickel-oxine-chloroforme.

## ZUSAMMENFASSUNG

Mit Hilfe der in einer früheren Veröffentlichung mitgeteilten Gleichungen wurde der Verlauf der Extraktion folgender Systeme verfolgt: Kupfer-Oxin-Chloroform und Nickel-Oxin-Chloroform.

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## SEPARATION OF ANTIMONY(V) FROM IRON(III), COPPER(II), COBALT(II) AND CADMIUM(II) BY ION-EXCHANGE

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In view of the difficulties usually associated with the conventional method of separation of antimony by precipitation as sulphide<sup>1</sup>, a simpler rapid method was desirable. In a previous communication<sup>2</sup>, a solvent extraction method for separating macro quantities of antimony(V) from nickel(II), chromium(III), lead(II), tin (IV), mercury(II) and small amounts of copper(II) was described. Iron(III), cobalt(II),

*References p. 410*

cadmium(II) and large quantities of copper(II) interfered with this method. It has now been found possible to separate these interfering cations from antimony(V) with the help of a cation-exchange resin (Zeo-Carb-225).

Separation of mixtures of antimony and other cations by ion-exchange resins has been reported in a few cases; none of these is useful in solving the present problem. LUR'E AND FILIPPOVA<sup>3</sup> separated zinc, aluminium, molybdenum, tungsten and antimony (from elements, e.g. Cu, Fe, which form basic hydroxides) by first adsorbing them all on a cation-exchanger (Wolfatit-P) and then eluting them with caustic soda solution of different concentrations. The same cation-exchanger retained antimony and tin from dilute acid solution but allowed arsenic to pass quantitatively<sup>4</sup>. It was also used for the separation of bismuth from antimony from 6% ammonium thiocyanate solution in 1 *N* H<sub>2</sub>SO<sub>4</sub>; this separation was very sensitive to thiocyanate concentration.

Anion-exchange resins have also been used in some cases. SMITH AND REYNOLDS<sup>5</sup> separated tracer quantities of <sup>124</sup>Sb(V), <sup>113</sup>Sn(IV) and <sup>125</sup>Te(IV) by adsorption on a Dowex-1 resin and subsequent elution with 0.1 *M* oxalic acid followed by *M* H<sub>2</sub>SO<sub>4</sub>. More recently, KLEMENT<sup>6</sup> claimed to have effected an excellent separation of arsenate from antimonate (as their soluble potassium salts) by adsorbing the former quantitatively on a strongly basic anion-exchanger in the sulfate form; but a considerable amount of potassium hydroxide had to be used to free the column from antimonate which was collected in the effluent.

In the present case we were concerned mainly with the determination of antimony in insoluble heavy metal antimonates. These can be dissolved in mineral acids, but the high acidity which is necessary to prevent hydrolysis of antimony(V) prevents adsorption on a cation exchanger. In presence of a complexing agent for antimony, the excess of mineral acid may be avoided. With a tartaric acid solution, MARCZENKO<sup>7</sup> was able to adsorb copper quantitatively on Wolfatit-P from a mixture with antimony and tin; he reported that 1–3% of antimony was also retained by the resin. Working with Zeo-Carb-225, we have found that retention of antimony(V) depends on the amount of tartaric acid present. With an excess of tartaric acid, copper(II), iron(III), cobalt(II) or cadmium(II) could be completely adsorbed on the resin, with the quantitative exclusion of antimony(V). Based on these observations, a method has been worked out for quantitative separation of antimony from any of the above cations.

#### EXPERIMENTAL

*Antimony stock solution.* Approximately 11.0 ml of SbCl<sub>5</sub> (B.D.H. reagent) was dissolved in 250 ml of 10% tartaric acid solution (w/v). The solution was filtered and stored in a closed bottle provided with a semi-micro delivery burette. Definite volumes of solution were taken out and their antimony content determined iodometrically.

*20% Tartaric acid solution.* 50 g of AnalaR tartaric acid was dissolved in 250 ml distilled water.

Solutions containing the other metal ions were prepared from AnalaR or Mercks reagents. The metal contents were verified by conventional methods; copper was determined by the iodometric method, iron by dichromate titration and cobalt and cadmium gravimetrically as their pyridine–thiocyanate complexes.

Solutions for percolation through the resin column were prepared by mixing together definite amounts of antimony stock solution and 20% tartaric acid solution. The mixture was passed through the resin column (Zeo-Carb-225 in H<sup>+</sup> form) at the rate of 30–40 drops per min. The resin column was then washed several times with distilled water and the washings were collected with the effluent, which was analysed for antimony. In the case of mixtures, the solutions were

prepared from antimony stock solution, tartaric acid solution and the relevant metal ion solutions. After separation of antimony, the adsorbed cation was eluted by passing hydrochloric acid solutions of known strength through the resin. In the eluate the metals were determined by the methods mentioned above.

## RESULTS AND DISCUSSION

### *Effect of tartaric acid on retention of antimony(V) on Zeo-Carb-225*

The effect of varying amounts of tartaric acid on the retention of antimony(V) on the resin can be seen from Table I. As the amount of tartaric acid is increased,

TABLE I  
EFFECT OF TARTARIC ACID CONTENT ON RETENTION OF ANTIMONY(V)

Tartaric acid added g	Antimony		Antimony retained by resin %
	taken g	found g	
0.30	0.1115	0.1067	+ 4.30
0.80	0.1115	0.1100	+ 1.345
1.30	0.1115	0.1109	+ 0.54
1.80	0.1115	0.1121	— 0.54
2.30	0.1115	0.1115	0.00
4.60	0.2230	0.2230	0.00
9.20	0.4460	0.4458	+ 0.045

retention of antimony(V) on the resin decreases, and with an excess of tartaric acid all the antimony(V) passes through the resin column. The optimum amount of tartaric acid necessary to prevent adsorption of antimony(V) on the resin is 16 to 20 times the weight of the metal.

The above results can be explained by considering the formation of stable anionic antimony-tartrate complexes in presence of excess tartaric acid. To support this view, a solution containing 0.1115 g of antimony(V) and 2.30 g of tartaric acid was percolated through an anion-exchanger De-Acidite FF in the sulfate form; the antimony was taken up quantitatively by the resin.

### *Separation of antimony(V) from interfering cations*

Solutions containing known amounts of antimony(V), tartaric acid and varying amounts of one of the interfering elements under study (*viz.* Cu(II), Fe(III), Cd(II) and Co(II)) were percolated through the cation-exchanger, Zeo-Carb-225. The effect of varying the amount of the interfering cation with the tartaric acid and antimony(V) concentrations constant, and the feasibility of quantitative separation were studied. Copper(II), cobalt(II) and cadmium(II) could be quantitatively eluted with 2 *N* hydrochloric acid but iron(III) required 4–6 *N* acid. The results (Tables II–V) indicate that within the range investigated mixtures of antimony(V) with other cations could be satisfactorily analysed; the results were accurate to  $\pm 1\%$ . In all cases, 2.3 g of tartaric acid was used.

TABLE II  
DETERMINATION OF ANTIMONY(V) AND COPPER(II)

<i>Antimony taken</i> g	<i>Antimony found</i> g	<i>Error for</i> <i>antimony</i> %	<i>Copper taken</i> g	<i>Copper found</i> g	<i>Error for</i> <i>copper</i> %
0.1115	0.1121	+ 0.54	0.03116	0.03116	0.00
0.1115	0.1113	— 0.18	0.06232	0.06169	— 1.01
0.1115	0.1115	0.00	0.12150	0.12020	— 1.07
0.1115	0.1115	0.00	0.24300	0.24240	— 0.25
0.1115	0.1121	+ 0.54	0.48600	0.48600	0.00

TABLE III  
DETERMINATION OF ANTIMONY(V) AND IRON(III)

<i>Antimony taken</i> g	<i>Antimony found</i> g	<i>Error for</i> <i>antimony</i> %	<i>Iron taken</i> g	<i>Iron found</i> g	<i>Error for</i> <i>iron</i> %
0.1115	0.1118	+ 0.27	0.02888	0.02876	— 0.42
0.1115	0.1110	— 0.45	0.05776	0.05752	— 0.42
0.1115	0.1116	+ 0.09	0.11552	0.11610	+ 0.50
0.1115	0.1115	0.00	0.23104	0.23160	+ 0.24
0.1115	0.1121	+ 0.54	0.46208	0.46130	— 0.17

TABLE IV  
DETERMINATION OF ANTIMONY(V) AND COBALT(II)

<i>Antimony taken</i> g	<i>Antimony found</i> g	<i>Error for</i> <i>antimony</i> %	<i>Cobalt taken</i> g	<i>Cobalt found</i> g	<i>Error for</i> <i>cobalt</i> %
0.1115	0.1115	0.00	0.02875	0.02866	— 0.31
0.1115	0.1124	+ 0.81	0.05750	0.05680	— 1.22
0.1115	0.1106	— 0.81	0.11500	0.11540	+ 0.35
0.1115	0.1109	— 0.54	0.23000	0.23110	+ 0.48
0.1115	0.1113	— 0.18	0.46000	0.46280	+ 0.61

TABLE V  
DETERMINATION OF ANTIMONY(V) AND CADMIUM(II)

<i>Antimony taken</i> g	<i>Antimony found</i> g	<i>Error for</i> <i>antimony</i> %	<i>Cadmium taken</i> g	<i>Cadmium found</i> g	<i>Error for</i> <i>cadmium</i> %
0.1115	0.1105	— 0.90	0.0422	0.0413	— 2.13
0.1115	0.1111	— 0.36	0.0844	0.0840	— 0.47
0.1115	0.1118	+ 0.27	0.1688	0.1694	+ 0.36
0.1115	0.1111	— 0.36	0.3376	0.3365	— 0.33
0.1115	0.1118	+ 0.27	0.6752	0.6792	+ 0.59

It was observed that under similar conditions, nickel(II), chromium(III) or lead(II) is also taken up selectively from its mixture with antimony(V) by Zeo-Carb-225, but mercury(II) and tin(II and IV) escape adsorption. As we had earlier found a suitable solvent extraction method<sup>2</sup> for this separation, detailed data on these mixtures are not presented.

## CONCLUSION

The results obtained indicate that in presence of tartaric acid iron(III), cobalt(II), copper(II), cadmium(II), nickel(II), chromium(III) and lead(II) do not form complexes sufficiently stable to escape retention on Zeo-Carb-225 ( $H^+$  form) while antimony(V) forms stable anionic complexes which are not taken up by the resin. Mercury(II), and tin(II and IV) cannot be separated from antimony(V) by this method.

## PROPOSED METHOD FOR ANALYSIS OF ANTIMONATES

Decompose 0.20 to 0.40 g of antimonate with conc. hydrochloric acid. Add dilute sodium hydroxide solution to neutralize the acid. Add the calculated amount of tartaric acid (any precipitate first formed must be dissolved completely). Percolate the solution slowly through a Zeo-Carb-225 resin column (10 g resin in  $H^+$  form). Wash the column several times with distilled water and collect the washings with the effluent. Analyse the effluent for antimony by the iodometric method. Elute the cations on the resin with a hydrochloric acid solution of the required strength and analyse the eluate for the metal by conventional methods.

## SUMMARY

With excess of tartaric acid, antimony(V) forms a stable anionic complex that completely escapes adsorption on a cation-exchange resin, Zeo-Carb-225, while Cu(II), Fe(III), Co(II) or Cd(II) is quantitatively retained. Antimony(V) can be separated from these ions in this way.

## RÉSUMÉ

Une méthode est proposée pour la séparation de l'antimoine(V) d'avec le cuivre, le fer(III), le cobalt et le cadmium, au moyen d'une résine d'échange de cations. L'antimoine doit être complexé au préalable par l'acide tartrique.

## ZUSAMMENFASSUNG

Antimon lässt sich in Gegenwart von Weinsäure von Kupfer, Eisen (III), Kobalt und Cadmium mit Hilfe eines sauren Ionenaustauschers abtrennen.

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## HETEROMETRIC MICRO-DETERMINATION OF TRACES OF IRON IN THIOCYANATE SOLUTIONS BY TITRATION WITH NITRON

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## INTRODUCTION

In the present paper a heterometric method is described for a very rapid determination of traces of ferric iron (0.05–0.08 mg in 20 ml of solution) in solutions containing *ca.* 99.9% of the following cations:  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Th}^{+4}$  or  $\text{Ce}^{+3}$ . The same quantity of iron could be determined in the presence of the following ions:  $\text{Ni}^{+2}$  ( $\sim 99.8\%$ ),  $\text{Pb}^{+2}$  (99.5%),  $\text{Sb}^{+3}$  (99.15%),  $\text{MoO}_4^{-2}$  (99.1%),  $\text{VO}_3^-$  (98.4%),  $\text{WO}_4^{-2}$  (96%) and  $\text{Cu}^{+2}$  (98.7%). A titration usually took *ca.* 5 minutes. In most cases the error was 1% or less, but exceptionally it amounted to *ca.* 3%.

The method is based on the quantitative precipitation of traces of ferric iron in concentrated solutions of thiocyanate by means of nitron.

## EXPERIMENTAL

The same working conditions were observed as in previous heterometric investigations. A deep red Corning filter (No. 2408) was always used.

a. A *M* ferric chloride stock solution was prepared from Baker "Analyzed" reagent; this was then gradually diluted with hydrochloric acid solution, so that the latter always had a molarity 10 times higher than that of the iron. The dilute iron solutions were freshly prepared at frequent intervals.

b. An aqueous nitron stock solution (0.01 *M*) was prepared as follows: 0.7802 g of nitron (M.W. 312.16, Eastman Organic Chemicals, for chemical purposes) and 7 ml of *N* acetic acid were dissolved in water to give 250 ml of aqueous solution. The dilute solutions were prepared from this solution every few days. The solutions of nitron were kept in dark brown bottles. The stock solution remained unchanged for months. All other chemicals used were either AnalaR or chemically pure reagents.

## RESULTS AND DISCUSSION

In Table I a selection of the experiments is given. A blank experiment was carried out by titrating the concentrated thiocyanate solution with nitron in the absence of iron; a slight white turbidity formed but this never interfered with the titrations. Table I indicates the highest concentration of the foreign metal which may be present without seriously affecting the titration of iron. In all titrations a horizontal maximum density line was obtained (Fig. 1) after the first maximum density point (= end-point). The flocculent precipitate obtained had a brick red colour. The molar ratio of  $[\text{Fe}^{+3}]:[\text{N}]$  (*N* = nitron) at the end-point was always 1:6.6. The precipitation of small amounts of iron depended on the concentration of thiocyanate in the solution. Thus, practically no precipitation occurred in 0.1 *M* thiocyanate solution

TABLE I

GENERAL COMPOSITION:  $a$  ml  $mM$   $FeCl_3$  +  $b$  ml  $N$   $HCl$  +  $c$  ml  $2 M$   $KCNs$  +  $d$  ml supplements + ad 20 ml  $H_2O$  +  $x$  ml  $nM$  nitron  
Content: 0.05–0.084 mg iron.  $T = 20^\circ$ . Red filter; Corning No. 2408

Expt. No.	$FeCl_3$		Supplements	% $Fe$	Molarity	Nitron		Maximum density value	% error	Titration time in min.
	ml	$mM$				Initial ppt. at ml	End-point at ml			
1	3	0.0005			0.0033	3.8				
2	3	0.0005			0.0033	1.2	i/c 2.90 h	0.46	2.8	10
3	3	0.0005			0.0033	0.6	i 2.94 h	0.68	1.5	5
4	3	0.0005			0.0033	0.6	i/c 3.00 h	0.72	0.5	5
5	3	0.0005			0.0033	0.6	i 3.00 h	0.77	0.5	5
6	3	0.001			0.005	0.0	i 4.00 h	>0.95		10
7	4	0.00025			0.0033	0.6	i 2.03 h	0.44	2.0	6
8	3	0.0005			0.0033	1.0	i 4.00 h	0.71	0.5	6
9	3	0.0005	0.2 ml $M$ $H_3PO_4$		0.0033	0.4	i/c 3.00 h	0.75	0.5	5
10	4	0.0005	0.5 ml $M$ $H_3PO_4$		0.005	0.6	i 2.70 h	0.81		5
11	4	0.00025	0.5 ml $M$ $H_3PO_4$		0.0033	0.8	i 2.03 h	0.42	2.0	8
12	3	0.0005	1 ml $M$ $Nag$ -citrate + 5 ml 2 $M$ $NH_4Cl$		0.0033	0.6	i 2.95 h	0.65	1.2	5
13	3	0.0005	1 ml $M$ $Nag$ -citrate + 5 ml 2 $M$ $NH_4NO_3$		0.0033	1.0	i 3.00 h	0.57	0.5	5
14	3	0.0005	1 ml $M$ $Nag$ -citrate		0.0033	0.6	i 3.01 h	0.62	0.5	5
15	3	0.0005	2 ml $M$ $CaCl_2$	0.1	0.0033	0.6	i 3.00 h	0.74	0.5	5
16	3	0.0005	3 ml 3 $M$ $AlCl_3$	0.04	0.0033	0.4	i 3.00 h	0.93	0.5	5
17	3	0.0005	5 ml $M$ $CrCl_3$	0.04	0.0033	0.4	i 2.98 h	0.57	0.2	4
18	3	0.0005	5 ml 2 $M$ $MnCl_2$	0.02	0.0033	0.6	i 3.02 h	0.78	0.7	4
19	3	0.0005	5 ml $M$ $CaCl_2$ + 1 ml $M$ $Nag$ -citrate	0.05	0.0033	0.6	i 2.98 h	0.77	0.2	5
20	3	0.0005	5 ml $M$ $BaCl_2$ + 1 ml $M$ $Nag$ -citrate	0.02	0.0033	0.4	i 2.98 h	0.76	0.2	5
21	3	0.0005	5 ml 2 $M$ $MgCl_2$ + 1 ml $M$ $Nag$ -citrate	0.04	0.0033	0.4	i 2.90 h	0.77	2.8	5
22	3	0.0005	1 ml $M$ $Zn(NO_3)_2$ + 1 ml $M$ $Nag$ -citrate	0.15	0.0033	0.2	i 3.10 h	0.53	3.8	7
23	3	0.0005	5 ml $M$ $CrCl_3$ + 1 ml $M$ $Nag$ -citrate	0.04	0.0033	0.4	i 3.00 h	0.52	0.5	5
24	3	0.0005	3 ml $M$ $Al(NO_3)_3$ + 1 ml $M$ $Nag$ -citrate	0.12	0.0033	0.4	i 3.00 h	0.82	0.5	5
25	3	0.0005	5 ml 2 $M$ $MnCl_2$ + 1 ml $M$ $Nag$ -citrate	0.02	0.0033	0.2	i 3.10 h	0.75	3.8	6
26	3	0.0005	1 ml $M$ $Ni(NO_3)_2$ + 1 ml $M$ $Nag$ -citrate	0.17	0.0033	0.4	i 2.98 h	0.69	0.2	5
27	3	0.0005	1 ml 0.01 $M$ $Co(NO_3)_2$ + 1 ml $M$ $Nag$ -citrate	12.3	0.0033	0.4	i 2.98 h	1.00	0.2	5
28	3	0.0005	1 ml 0.1 $M$ $Na_2MoO_4$ + 1 ml $M$ $Nag$ -citrate	0.86	0.0033	0.8	i 3.08 h	0.69	3.2	5
29	3	0.0005	1 ml 0.1 $M$ $NaVO_3$ + 1 ml $M$ $Nag$ -citrate	1.6	0.0033	0.4	i 2.95 h	0.87	1.2	5
30	3	0.0005	1 ml 0.01 $M$ $Na_2WO_4$ + 1 ml $M$ $Nag$ -citrate	4.3	0.0033	0.4	i 3.00 h	0.48	0.5	8
31	3	0.0005	1 ml $M$ $Cd(NO_3)_2$	0.07	0.0033	0.6	i 3.00 h	0.75	0.5	15
32	3	0.0005	1 ml 0.1 $M$ $Pb(NO_3)_2$ + 1 ml $M$ $Nag$ -citrate	0.5	0.0033	0.4	i 3.00 h	0.78	0.5	5
33	3	0.0005	1 ml 0.08 $M$ $SbCl_3$ + 1 ml $M$ $Nag$ -citrate	0.85	0.0033	0.4	i 2.90 h	0.78	2.8	6
34	3	0.0005	0.5 ml 0.2 $M$ $Cu(NO_3)_2$ + 1 ml $M$ $Nag$ -citrate	1.3	0.0033	0.4	i 3.00 h	0.88	0.5	17
35	3	0.0005	0.5 ml 0.2 $M$ $Cu(NO_3)_2$ + 0.5 ml $M$ $H_3PO_4$	1.3	0.0033	0.4	i 3.00 h	0.88	0.5	5
36	3	0.0005	5 ml 0.1 $M$ $Th(NO_3)_4$ + 1 ml $M$ $Nag$ -citrate	0.07	0.0033	0.6	c 2.95 h	0.69	1.2	5
37	3	0.0005	5 ml 0.1 $M$ $Ce(NO_3)_3$ + 1 ml $M$ $Nag$ -citrate	0.12	0.0033	0.6	i 2.95 h	0.68	1.2	5

i = intersection point; h = horizontal maximum density line; > = density increase after the end-point; c = contact point.

(Expt. 1); the minimum concentration necessary for quantitative reaction was 0.5 *M* (Expt. 1-5). The reaction with nitron always occurred instantaneously. It must therefore be assumed that this reaction is of an ionic character and that the nitron acted somehow as cation. However, it seems unlikely that 6 molecules of nitron per 1 iron atom were necessary to give the insoluble ferric-nitron-thiocyanate salt and the insoluble compound obtained may be of a more complex nature.

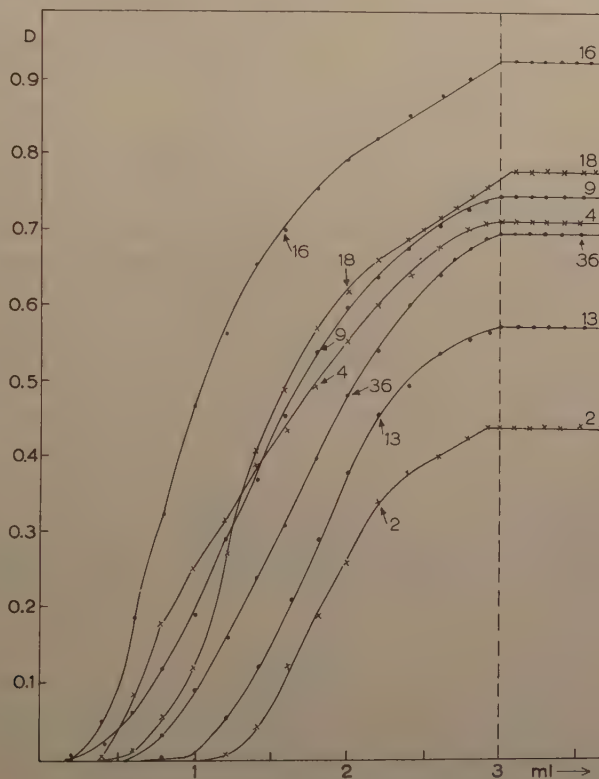


Fig. 1. Titrations of iron chloride with nitron.

Some titrations of nitron with iron chloride solutions were also carried out. The results were not so clear as in the reverse titrations, but again in most cases the above molar ratio of iron to nitron was found at the end of the titration.

When iron thiocyanate was titrated with nitron in hydrochloric acid solution, the titrant had to be added almost continuously, otherwise the density values measured soon decreased again. The same thing occurred with the maximum density values measured, which could not be stabilized. This phenomenon was apparently caused by the character of the "primary reaction" measured, and the tendency of the insoluble compound to be rearranged and redissolved. Many experiments were carried out in order to stabilize the readings of the galvanometer. When the influence of different supplements on the reaction was studied, it was found that citric acid acted very favourably in stabilizing the measurements. Therefore all further experiments

were carried out with the addition of trisodium citrate to the hydrochloric acid solution. Some titrations were repeated with and without citric acid. In some cases, merely the presence of a foreign metal salt in concentrated solution (*e.g.* aluminium chloride, Expt. 16) was sufficient to stabilize the readings. The citric acid complexed the iron *before* it reacted with the nitron and so possibly the uncomplexed ferric iron interfered with the insoluble compound first formed. This is probably not the only reason, as the end-point density values decreased rapidly in the absence of citric acid. The favourable influence of the concentrated foreign salt (Expt. 16) may be caused partly by an increase in viscosity which weakened the activity of the primary compound. The titration time and the maximum density values obtained were usually similar whether the citric acid was present or not.

The concentration of iron in the solution had to be 0.0001–0.0002 *M*. Within these concentrations the maximum density values were proportional to the amount of iron present (Expt. 4 and 7). As experiments 9–11 indicate, the strong hydrochloric acid could be replaced by phosphoric acid without affecting the maximum density value or the end-point; after the end-point, a horizontal maximum density line was always obtained. The presence of a large excess of ammonium chloride or nitrate (Expt. 12 and 13) had hardly any influence on the results although the maximum density value was slightly depressed. The results of some titrations in the presence of large amounts of foreign salts but in the absence of citric acid, are presented in Expt. 15–18. From these and the following experiments (Expt. 19–25), it can be seen that less than 0.1 mg of ferric iron (*ca.* 0.1%) in 20 ml of solution can be determined in the presence of 99.9% of  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Th}^{+4}$  and  $\text{Ce}^{+3}$ . Thus, it is possible to determine traces of iron directly in concentrated solutions of salts of the calcium-barium and the ammonium sulphide groups. This reaction could probably also be used in qualitative analysis for the detection of iron in the presence of the above cations.

#### METHOD

Less than 0.1 mg of ferric iron (conc.  $1-2 \times 10^{-4}$  *M*) in 20 ml of an aqueous solution is titrated with a 0.0025–0.0033 *M* solution of nitron. The test solution must contain 5 ml of 2 *M* KCNS, 1 ml of *M* citric acid and 0.5 ml of *N* HCl.

#### SUMMARY

Traces of ferric iron were determined heterometrically in concentrated solutions of potassium thiocyanate by titration with nitron. The solutions could contain 99.9% of the following cations:  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Th}^{+4}$ ,  $\text{Ce}^{+3}$  or 99% of  $\text{Ni}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Mo}^{+6}$ ,  $\text{V}^{+5}$  and W. A titration usually lasted 5 min and in most cases the error was *ca.* 1%. The molar ratio of  $[\text{Fe}]:[\text{nitron}]$  was always equal to 1:6.6.

#### RÉSUMÉ

Une méthode rapide, par hétérométrie, est proposée pour le dosage de traces de fer(III). Le titrage s'effectue au moyen de nitron, dans des solutions concentrées de thiocyanate de potassium.

#### ZUSAMMENFASSUNG

Es wird eine „heterometrische“ Methode beschrieben zur raschen Bestimmung von Spuren von Eisen(III) durch Titration mit Nitron in kaliumthiocyanathaltiger Lösung.

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## GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

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N-Benzoylphenylhydroxylamine was recommended for the precipitation and determination of metals<sup>1,2</sup> and has been used<sup>3</sup> for the gravimetric estimation of molybdenum. SHOME<sup>1</sup> observed that the reagent forms insoluble complexes with thorium, cerium and other metal ions in aqueous solutions. In the present investigation thorium and cerium have been determined with benzoylphenylhydroxylamine; thorium has been separated from cerium by making use of the fact that thorium is precipitated at pH 5.0 whilst cerous ion is precipitated at pH 7.0.

### EXPERIMENTAL

#### *Solutions of metals*

Standard solutions of thorium nitrate and ceric ammonium nitrate were prepared to contain respectively 2.84 mg of thorium dioxide and 2.408 mg of cerium dioxide per ml.

All the chemicals employed were of A.R. quality.

### DETERMINATION OF THORIUM

A known amount of the thorium nitrate solution (25 to 30 ml) was diluted with distilled water to 250 ml, and 10% ammonium acetate solution was added to adjust the pH to about 5.0; the pH value was ascertained with indicator paper. Benzoylphenylhydroxylamine (0.3 to 0.4 g) in alcohol (10 to 15 ml) was then added with constant stirring. The white precipitate was occasionally stirred for 15 min, filtered, washed with water, ignited to dioxide in a porcelain crucible and weighed.

The results (Table I) show that thorium is precipitated quantitatively with benzoylphenylhydroxylamine between pH 4.5 and 5.5 and the metal can be determined by igniting the precipitate to thorium dioxide and weighing.

TABLE I

DETERMINATION OF THORIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Thorium dioxide		Error g
taken (g)	found (g)	
0.0710	0.0705	— 0.0005
0.0738	0.0733	— 0.0005
0.0767	0.0761	— 0.0006
0.0794	0.0790	— 0.0004
0.0852	0.0846	— 0.0006

pH of solutions = 4.5 to 5.5

## DETERMINATION OF CERIUM

A known quantity of the ceric ammonium nitrate solution (25 to 30 ml) was heated to boiling and 5% hydroxylamine hydrochloride solution (10 ml) was added to reduce the ceric ions. The solution was diluted to 250 ml, allowed to cool and 10 ml of the hydroxylamine hydrochloride solution was added to prevent oxidation of the cerous ions during the subsequent precipitation. Benzoylphenylhydroxylamine (0.3 to 0.4 g) in alcohol (10 to 15 ml) was then added and the pH of the solution was raised to about 7.0 by adding 1*N* ammonium hydroxide solution to complete the precipitation. The white precipitate was occasionally stirred for 30 min, filtered, washed, ignited to cerium dioxide and weighed.

TABLE II

DETERMINATION OF CERIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Cerium dioxide		Error g
taken (g)	found (g)	
0.0602	0.0596	— 0.0006
0.0626	0.0629	+ 0.0003
0.0650	0.0649	— 0.0001
0.0674	0.0678	+ 0.0004
0.0722	0.0719	— 0.0003

pH of solutions = 6.5 to 7.5

The precipitation of trivalent cerium (Table II) with benzoylphenylhydroxylamine was complete between pH 6.5 and 7.5; above pH 7.5 the reagent solution gradually assumed a red colour. The ceric ions could be precipitated with benzoylphenylhydroxylamine at pH. 5.0, but the ceric complex was difficult to filter because of its gelatinous nature.

## SEPARATION OF THORIUM AND CERIUM

A mixture containing known amounts of the thorium and ceric solutions was heated to boiling and hydroxylamine hydrochloride solution was added as above. The solution was cooled, diluted to 250 ml and more hydroxylamine hydrochloride

solution (10 ml) was added. The pH of the solution was then raised to about 5.0 and thorium precipitated as described above. The precipitate was filtered and immediately washed with a freshly prepared 0.1% hydroxylamine hydrochloride solution and finally with distilled water. The precipitate was dried and ignited to thorium dioxide. The filtrate and washings were evaporated to about 250 ml and hydroxylamine hydrochloride solution (10 ml) was added to prevent the formation of any ceric complex. The cerous ion was then determined as described above.

The results (Table III) show that thorium can be separated from cerium and the individual metals determined by means of benzoylphenylhydroxylamine. During the concentration of the combined filtrate and washings, solid organic matter appeared, which was probably formed by the prolonged heating of the reagent solution in air.

TABLE III

SEPARATION OF THORIUM AND CERIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Mixture No.	Thorium dioxide		Cerium dioxide	
	taken g	found g	taken g	found g
1	0.0852	0.0849	0.0602	0.0598
2	0.0909	0.0907	0.0626	0.0628
3	0.0794	0.0787	0.0650	0.0652
4	0.0767	0.0768	0.0722	0.0717
5	0.0625	0.0629	0.0938	0.0941

## ACKNOWLEDGEMENT

One of us (S. K. S.) is indebted to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a scholarship.

## SUMMARY

Benzoylphenylhydroxylamine has been used for the precipitation of thorium and trivalent cerium; the precipitates are ignited to the corresponding metal dioxide and weighed. Ceric ions are reduced before precipitation. The gravimetric separation of thorium and cerium is effected by precipitation at different pH values.

## RÉSUMÉ

La benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du thorium et du cérium. Il est possible de séparer ces deux éléments en effectuant la précipitation à des pH différents.

## ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Thorium und Cer kann Benzoylphenylhydroxylamin verwendet werden. Bei Einhaltung bestimmter pH-Werte lassen sich die beiden Metalle getrennt fällen.

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## A SPECIFIC METHOD FOR THE DETERMINATION OF URANIUM IN ORES BY CATHODE RAY POLAROGRAPHY

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### INTRODUCTION

In recent years polarographic procedures have been extensively applied to the determination of uranium in ores. Among the many base electrolytes employed may be mentioned the acid-tartrate method of LEWIS AND OVERTON<sup>1,2</sup>, the acid-oxalate method of LEGGE<sup>3</sup>, and the ascorbic acid method of SUSIC<sup>4</sup>. While some doubt appears to exist regarding the selectivity of these base electrolytes towards uranium<sup>5</sup>, the acid-tartrate and the ascorbic acid base electrolytes appear to be the most selective of those available. A systematic study of interferences in these two methods indicated, however, that they may not, in general, be directly applied to the determination of uranium in ores. Considering the low concentrations of uranium frequently present in these ores, and the wide variety of foreign elements associated with uranium, it is usually necessary to separate the uranium from the bulk of the impurities. Vanadium, in particular, interferes seriously in most polarographic determinations of uranium<sup>6,7</sup>, and is also difficult to completely separate from uranium prior to the determination<sup>8</sup>.

The methods most commonly used for the purification of the uranium solution are chromatography<sup>9</sup>, solvent extraction<sup>10</sup>, and ion-exchange<sup>11</sup>. Chromatography and solvent extraction suffer from the disadvantage that large amounts of organic solvents are employed which must be completely removed before the polarographic determination. The anion-exchange separation of uranium on a strongly-basic resin from dilute sulphate solutions<sup>11</sup> is apparently the most selective available, but difficulty was experienced in this laboratory in obtaining complete recovery and good separation of the uranium at the same time. A mercury cathode separation of uranium appears ideal where a polarographic finish to the determination is contemplated, since a large number of foreign elements are removed, the operation is simple and rapid, and the solution comes in contact only with glass, mercury and platinum. In this paper a procedure is described, using a small mercury cathode cell, which allows the uranium to be separated in less than one hour by the "constant current" electrolysis technique. A base electrolyte has been developed in which elements not removed by the mercury cathode electrolysis, do not interfere in the polarographic determination of uranium. This base electrolyte is considered the most selective yet developed for uranium, and combined with a previous mercury cathode separation, the method appears specific for uranium in ores processed in this country.

### APPARATUS

A linear-sweep cathode ray polarograph equipped with an electrode stand and

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constant temperature water bath, from Southern Instruments Computer Division, Surrey, England, was used for the experimental work. This instrument is of the DAVIS type<sup>12</sup>, with a voltage sweep rate of 0.3 V per sec, a sweep time of 2 sec and a delay period of 5 sec. A polarographic cell employing a mercury pool anode was used throughout. All polarographic measurements were made at 25°.

### Mercury cathode electrolysis cell

This cell is illustrated in Fig. 1. An aliquot of the solution may be withdrawn from the cell without interrupting the electrolysis by means of a pipette inserted through the air-condenser socket. The surface of the mercury may be stirred with a magnetic stirrer, or alternatively, by vibration.

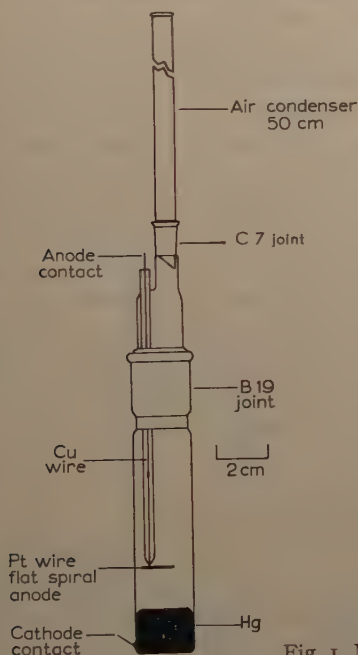


Fig. 1. Mercury cathode cell.

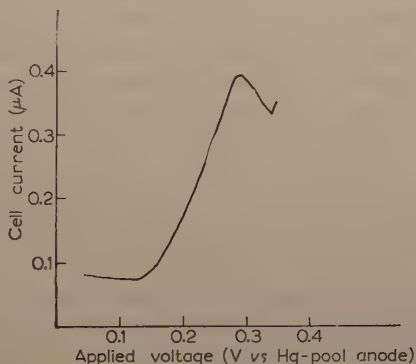


Fig. 2. Polarography of  $2 \cdot 10^{-5} M$  uranium in "mixed" base electrolyte.

### REAGENTS

#### Base electrolyte stock solution

Dissolve the following reagents in demineralized water, and dilute to 1 l: tribasic ammonium citrate (194 g), citric acid monohydrate (84 g), ammonium oxalate monohydrate (14.2 g), disodium ethylene diamine tetraacetate dihydrate (37 g), sodium chloride (5.85 g). The chemicals used should be the purest grade available.

This stock solution was purified by a controlled-potential mercury cathode electrolysis, using a cell of 1.5-l capacity<sup>13</sup>, a cylindrical platinum-gauze anode, and a silver-silver chloride reference electrode. The potential of the mercury cathode was maintained by a manually operated circuit at  $-0.8$  V *versus* the reference electrode for 5 h. The purified solution was filtered into a polythene storage bottle.

The pH of this solution should be 4.7 at 25°.

*1.0 M ascorbic acid*

High purity *l*-ascorbic acid from C.S.R. Chemicals Pty. Ltd., Sydney, was used for the preparation of this solution. Dissolve 17.6 g of ascorbic acid in water and dilute to 100 ml. This solution should be prepared fresh daily.

All other chemicals used were of A.R. quality.

## PROCEDURE FOR THE DETERMINATION OF URANIUM IN ORES

Weigh a suitable amount of the very finely ground ore directly into a small platinum dish. Add 5 ml of conc.  $\text{HNO}_3$  and 5 ml of 50%  $\text{H}_2\text{F}_2$ . Swirl gently, and evaporate the solution just to dryness. Add further 5-ml portions of  $\text{HNO}_3$  and  $\text{H}_2\text{F}_2$  and repeat the evaporation until solution of the ore is complete. Add sufficient 72%  $\text{HClO}_4$  to make the sample solution, when diluted to volume, 0.1 *N* in  $\text{HClO}_4$ . Heat to fumes of  $\text{HClO}_4$  for a few min, then cool and dilute to volume with water in a volumetric flask. The sample solution should be between  $10^{-5}$  and  $2 \cdot 10^{-4}$  molar in uranium.

Transfer about 15 ml of solution to the mercury cathode cell. Electrolyse at 6–9 V (1.5 A) for 40–60 min. Remove the air condenser and withdraw a 5-ml aliquot of the solution while electrolysis is still proceeding. Transfer to a small, dry, stoppered flask and cool under a tap to room temperature. Pipette a 2-ml aliquot into a 10-ml volumetric flask. Add 2 ml of 1.0 *M* ascorbic acid, one drop of 5 *N* NaOH, and mix. Add 5 ml of the base electrolyte stock solution and dilute to volume with water. Immediately transfer about 3 ml of this solution to a polarographic cell and pass nitrogen gas through the solution at a slow rate for 5–10 min. Using a start potential of zero volts, measure the peak current occurring at about  $-0.28 \text{ V v. Hg pool anode}$ . Under the same conditions record the peak current due to a standard uranyl perchlorate solution of approximately the same concentration as the unknown. After correction of the results for residual current, which should be less than  $0.01 \mu\text{A}$ , the uranium content of the ore may be calculated.

## THE MERCURY CATHODE SEPARATION

Using the cell, and the procedure described, it was found that large amounts of copper, iron, molybdenum, tin and other metals could be removed from the solution in less than 30 min. It is interesting to note that if the uranium concentration is kept below  $5 \cdot 10^{-4} \text{ M}$  no net reduction of uranium occurs during the electrolysis in 0.1 *N*  $\text{HClO}_4$ . This phenomenon does not occur with dilute uranium solutions in 0.1 *N*  $\text{H}_2\text{SO}_4$  nor with more concentrated uranium solutions in 0.1 *N*  $\text{HClO}_4$ . Here considerable reduction occurs during electrolysis, and the solution must be reoxidized before the polarographic determination is carried out. It is believed the presence of a small amount of oxidizing agent, *e.g.* chlorine formed by the decomposition of some perchloric acid, is sufficient to reoxidize the dilute uranium solution.

## COMPOSITION OF THE BASE ELECTROLYTE

Of the elements which remain in solution with uranium after a mercury cathode electrolysis, vanadium, titanium and tungsten are most likely to interfere in the subsequent polarographic determination of uranium. The interference of vanadium has been shown<sup>6</sup> to be partly due to oxidation of pentavalent uranium by tetravalent vanadium:



The regenerated uranyl ions are then available for further reduction, leading to erroneously high diffusion currents. Since considerable amounts of vanadium are commonly encountered in uranium ores, this interference is serious. Many previously published base electrolytes for uranium were investigated, but none could tolerate even moderate amounts of vanadium.

It is known<sup>14,15</sup>, that vanadium, particularly VO<sup>+2</sup> and V<sup>+3</sup>, forms strong complexes with ethylenediaminetetraacetic acid (EDTA). In a base electrolyte consisting of ascorbic acid and EDTA no reduction wave for vanadium is evident, and vanadium up to 200 times the uranium concentration may be present before interference occurs. This base electrolyte is quite selective towards uranium, but unfortunately even small amounts of titanium interfere. By adding citric acid and maintaining the pH at 4-5, the titanium reduction wave is shifted to a very negative potential, and an ascorbate-EDTA-citrate base electrolyte will tolerate large concentrations of titanium. In this medium, however, a double uranium wave is obtained, the first wave representing the reduction of the uranyl ion to the pentavalent state, and the second wave, occurring at a slightly more negative potential, is probably due to disproportionation of the pentavalent uranium:

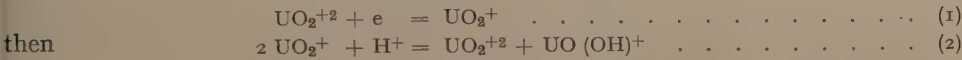


TABLE I  
INTERFERENCE OF DIVERSE CATIONS IN THE ASCORBATE, TARTRATE AND "MIXED" BASE  
ELECTROLYTES FOR THE DETERMINATION OF URANIUM

Showing the concentration level, 100 : 1, 10 : 1, 1 : 1 or 0.1 : 1 corresponding to foreign element : uranium, at which interference first occurs. Uranium conc. in all cases 8 · 10<sup>-4</sup>%

<i>Ion</i>	<i>Ascorbate</i>	<i>Tartrate</i>	<i>"Mixed"</i>
Al <sup>+3</sup>	nil	nil	nil <sup>b</sup>
As <sup>+3</sup>	nil	nil	nil
Bi <sup>+3</sup>	1 : 1	10 : 1	nil
Ca <sup>+2</sup>	nil	nil	nil
Cd <sup>+2</sup>	nil	nil	nil
Ce <sup>+4</sup>	nil	nil	nil
Co <sup>+2</sup>	nil	nil	nil
Cr <sup>+6</sup>	nil	1 : 1	10 : 1
Cu <sup>+2</sup>	1 : 1	0.1 : 1	0.1 : 1
Fe <sup>+3</sup>	nil	10 : 1 <sup>a</sup>	10 : 1
Mg <sup>+2</sup>	nil	nil	nil
Mn <sup>+2</sup>	nil	nil	nil
Mo <sup>+6</sup>	0.1 : 1	0.1 : 1	1 : 1
Ni <sup>+2</sup>	nil	nil	nil
Pb <sup>+2</sup>	0.1 : 1	nil	nil
Sb <sup>+3</sup>	100 : 1	100 : 1	nil
Sn <sup>+2</sup>	0.1 : 1	0.1 : 1	10 : 1 <sup>a</sup>
Te <sup>+6</sup>	0.1 : 1	nil	nil
Th <sup>+4</sup>	nil	nil	nil
Ti <sup>+4</sup>	100 : 1	1 : 1	nil
Tl <sup>+</sup>	10 : 1	100 : 1	1 : 1
V <sup>+5</sup>	1 : 1	0.1 : 1	nil
W <sup>+6</sup>	0.1 : 1	1 : 1	100 : 1
Zn <sup>+2</sup>	nil	nil	nil
Zr <sup>+4</sup>	nil	nil	nil

<sup>a</sup> peak potential altered;   <sup>b</sup> double wave obtained.

By adding a small amount of ammonium oxalate, a single uranium wave is again obtained, its height being equal to the sum of the two previous waves. The oxalate ion forms strong complexes with both hexavalent and tetravalent uranium<sup>16</sup>, and apparently accelerates reaction (2).

The final composition of the base electrolyte is then: 0.2 *M* ascorbic acid, 0.4 *M* ammonium citrate, 0.2 *M* citric acid, 0.05 *M* ammonium oxalate, 0.05 *M* EDTA and 0.05 *M* sodium chloride. The sodium chloride is added to enable a mercury-pool anode to be used.

While this base electrolyte is admittedly complex, this is no disadvantage, as the constituents, with the exception of ascorbic acid, are stable and compatible, and a concentrated stock solution may be prepared and stored indefinitely. Small variations in the composition of the base electrolyte do not affect the determination. If the uranium concentration is below  $10^{-4}$  *M*, a particularly well formed wave is obtained with a very flat base line (Fig. 2). With larger amounts of uranium the wave becomes drawn out and ill defined.

#### STUDY OF INTERFERENCES

Table I shows the effect of diverse ions in the ascorbate, acid-tartrate, and the citrate-oxalate - EDTA - ascorbate ("mixed") base electrolytes for the determination of uranium using a Cathode Ray polarograph and a Hg-pool anode.

The 1 *M* H<sub>2</sub>SO<sub>4</sub>, 0.05 *M* sodium tartrate base was prepared as directed by SHALGOSKY<sup>2</sup> (no maximum suppressor), and the ascorbate base was 0.5 *M* ascorbic acid containing 0.05 *M* sodium chloride and adjusted to pH 3.7. The final solutions contained  $8 \cdot 10^{-4}\%$  uranium, and  $8 \cdot 10^{-2}\%$ ,  $8 \cdot 10^{-3}\%$ ,  $8 \cdot 10^{-4}\%$ , and  $8 \cdot 10^{-5}\%$  respectively of the particular element for the concentration levels 100 : 1, 10 : 1, 1 : 1 and 0.1 : 1 element to uranium. The table shows the concentration level at which interference (2% error in peak current) first occurs.

Whenever possible the foreign elements were added as the perchlorates, prepared by solution of the element or its oxide in perchloric acid.

It may be seen from the table that Bi<sup>+3</sup>, Cr<sup>+6</sup>, Cu<sup>+2</sup>, Fe<sup>+3</sup>, Mo<sup>+6</sup>, Sn<sup>+2</sup>, Ti<sup>+4</sup>, V<sup>+5</sup> and W<sup>+6</sup> interfere seriously in the acid-tartrate method. Using the ascorbate base electrolyte at pH 3.7, Bi<sup>+3</sup>, Cu<sup>+2</sup>, Mo<sup>+6</sup>, Pb<sup>+2</sup>, Sn<sup>+2</sup>, Te<sup>+6</sup>, Tl<sup>+</sup>, V<sup>+5</sup> and W<sup>+6</sup> interfere seriously. With the "mixed" base Cr<sup>+6</sup>, Cu<sup>+2</sup>, Fe<sup>+3</sup>, Mo<sup>+6</sup>, Sn<sup>+2</sup> and Tl<sup>+</sup> interfere. Tungsten does not interfere if it is less than 50 times the uranium concentration. If more than 5 mg of aluminium is present in the final solution a double wave is obtained, presumably due to the removal of oxalate ions by Al<sup>+3</sup>. While iron is reduced completely by ascorbic acid, on the addition of the base electrolyte a ferric wave gradually reappears. This is probably due to the formation and oxidation of a ferrous-EDTA complex, which is known to be very rapidly oxidized by air<sup>17</sup>.

In addition to the cations shown, the "mixed" base electrolyte was found to be unaffected by large amounts of sulphate, chloride, nitrate and phosphate.

#### COMPARISON OF BASE ELECTROLYTES

Table II compares the peak potentials and sensitivities of the acid-tartrate, ascorbate and "mixed" base electrolytes at a uranium concentration of  $2 \cdot 10^{-5}$  *M*.

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It is seen that at the uranium concentration used, the "mixed" base electrolyte is somewhat more sensitive than the other two.

TABLE II

COMPARISON OF PEAK POTENTIALS AND SENSITIVITIES OF THE TARTRATE, ASCORBATE AND "MIXED" BASE ELECTROLYTES FOR THE DETERMINATION OF URANIUM

Base electrolyte	Peak potential in <i>V</i> versus Hg-pool anode (0.05 <i>M</i> chloride)	$K = ip/C \mu A/mmole/l^a$ for a $UO_2^{+2}$ concn. of $2 \cdot 10^{-5}$ moles/l
Tartrate	—0.38	13.4
Ascorbate	—0.27	13.0
"Mixed"	—0.28	14.1

<sup>a</sup> *ip* = peak current for *m* = 1.14 mg/sec

*t* = 6.5 sec

RELATIONSHIP BETWEEN URANIUM CONCENTRATION AND PEAK CURRENT

It may be seen from Table III that peak current is proportional to concentration in the "mixed" base electrolyte if the uranium concentration is below  $4 \cdot 10^{-5}$  *M*. Above this value the peak current becomes proportionally less, the reduction wave gradually assumes an irreversible nature, and the peak potential shifts to more negative values.

TABLE III

RELATIONSHIP OF PEAK CURRENT TO CONCENTRATION OF URANYL ION IN THE "MIXED" BASE ELECTROLYTE AT 25°

$UO_2^{+2}$ concn. ( <i>C</i> ) moles/l	Peak current <i>ip</i> $\mu A$	$K = ip/C \mu A/mmole/l$
$1 \cdot 10^{-3}$	9.80	9.80
$5 \cdot 10^{-4}$	5.11	10.3
$2 \cdot 10^{-4}$	2.22	11.1
$1 \cdot 10^{-4}$	1.21	12.1
$5 \cdot 10^{-5}$	0.658	13.2
$4 \cdot 10^{-5}$	0.559	14.0
$2 \cdot 10^{-5}$	0.282	14.1
$1 \cdot 10^{-5}$	0.142	14.2
$5 \cdot 10^{-6}$	0.0705	14.1
$2 \cdot 10^{-6}$	0.0280	14.0
$1 \cdot 10^{-6}$	0.0141	14.1
$5 \cdot 10^{-7}$	0.0070	14.0

ANALYSIS OF ORES

Table IV shows the results obtained on ten samples of uranium ores by the polarographic method described above. The results on ores No. 1–7 are compared with those obtained by an independent research organisation using the classical method consisting of a cellulose column separation of the uranium from nitric acid–ether solution, followed by spectrophotometric determination with hydrogen peroxide. Ores No. 8–10 were analysed fluorometrically by an independent laboratory.

In addition to uranium, ores No. 1–7 were found to contain silica (25–85%),

iron (5–65%), vanadium (0.2–2.0%), copper (0.05–0.2%), and small amounts of the following elements: Al, Pb, Cr, Ti, Mo, Ni, Ag, Au, Bi, W and Mn.

To test the precision of the procedure outlined, ten portions of ore No. 5 were carefully analysed. The results gave a standard deviation ( $n=1$ ) of 1.9%.

TABLE IV

APPLICATION OF THE "MIXED" BASE ELECTROLYTE POLAROGRAPHIC METHOD FOR URANIUM TO THE DETERMINATION OF URANIUM IN ORES

Ore No.	Reference method % $U_3O_8$	"mixed base" polarographic method % $U_3O_8$	Difference %
1	8.3	8.3	—
2	7.6	7.5	—1.3
3	0.72	0.73	+1.4
4	0.65	0.65	—
5	0.55	0.55	—
6	0.42	0.44	+4.8
7	0.34	0.35	+2.9
8	0.037	0.046	+24
9	0.020	0.025	+25
10	0.011	0.014	+27

## SUMMARY

A method is presented for the specific determination of uranium in ores by cathode ray polarography. The uranium is separated by a simple and rapid mercury-cathode electrolysis, then determined polarographically in a base electrolyte in which vanadium, titanium and tungsten do not interfere. Application of the method to the analysis of ten standard uranium ores is shown.

## RÉSUMÉ

Une méthode spécifique, par polarographie à rayons cathodiques, est proposée pour le dosage de l'uranium dans ses minerais. L'uranium est préalablement séparé par électrolyse sur cathode de mercure.

## ZUSAMMENFASSUNG

Es wird eine spezifische Methode beschrieben zur Bestimmung von Uran in Erzen durch Kathodenstrahlen-Polarographie nach elektrolytischer Abtrennung mit einer Quecksilberkathode.

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## THE POLAROGRAPHIC DETERMINATION OF CHROMIUM IN ALUMINUM ALLOYS

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## INTRODUCTION

The determination of chromium in aluminum alloys is based mainly on titrimetric or photometric methods. The only polarographic method found in the literature<sup>1</sup> entails a rather elaborate preparation of the sample; after dissolution of the sample in an acid mixture, it is twice evaporated to sulphuric acid fumes, and, in alloys containing more than 0.25% copper, copper is removed by prior electrolysis.

The development of a convenient polarographic method for the determination of chromium in aluminum alloys appeared desirable. The method proposed is based on dissolution of the alloy in a bromine water-sodium hydroxide mixture; subsequent filtration affords a simple separation of the hexavalent chromium from all the constituents of the alloy except those soluble in sodium hydroxide. Excess hypobromite is easily removed by the addition of ammonia solution to the filtered sample solution<sup>2</sup>, which may then be made up to volume and used directly for the polarographic determination of chromium.

The reduction of hexavalent to trivalent chromium in 1 *N* sodium hydroxide solution affords a well-developed polarographic wave<sup>3</sup>, which lends itself admirably to quantitative interpretation. Aluminum, titanium and zinc, the only constituents of the alloy accompanying the chromium in the filtered solution, do not interfere with this wave.

## EXPERIMENTAL

*Apparatus*

A Type E. Leeds Northrup Electro-Chemograph (pen recording polarograph) was used. Damping "2" was employed throughout.

Since the medium chosen for recording the polarograms was strongly alkaline, attacking the capillaries and making their frequent replacement necessary, methods of quantitative interpretation independent of the capillary characteristics were employed. The drop time, the amount of mercury flowing through the capillary and the height of the mercury column are, therefore, not reported. All samples were thermostatted at  $25^{\circ} \pm 0.1^{\circ}$  and de-aerated with purified nitrogen before the polarograms were recorded. 100-ml Pyrex glass beakers were used as polarographic cells, with a Lingane type<sup>4</sup> S.C.E. serving as reference electrode.

*Standard solutions and reagents*

1. Standard potassium dichromate solution (prepared by dissolving 0.2829 g of dried potassium dichromate in water and making up to 1 l. This solution contains 0.1 mg Cr per ml). 2. Bromine water, saturated. 3. Sodium hydroxide solution, conc. (prepared daily, by dissolving 30 g of sodium hydroxide in 50 ml of water). 4. Sodium hydroxide solution, 3%. 5. Ammonia solution (1 : 1). 6. Triton X-100 solution, 0.2%. (This is a non-ionic detergent, manufactured by Rohm and Haas Co., which served as maximum suppressor.) 7. British Chemical Standards Alloy, No. 263. This is a magnesium-aluminum alloy, containing 0.34% Cr, and also Cu, Mg, Si, Fe, Mn, Zn and Ti. 8. Aluminum metal, pure.

All reagents employed were of analytical quality.

*References p. 429*

## PROCEDURE

*Preparation of the sample solution*

0.250–0.500 g of the alloy, containing about 1 mg of chromium was weighed into a 100-ml Pyrex glass beaker; 10 ml of the saturated bromine water were added, followed by 5 ml of the conc. sodium hydroxide solution. After the initial effervescence had subsided, the mixture was heated gently to effect complete dissolution of the alloy and then boiled for 5 min. An additional portion of 5 ml of bromine water was added and the mixture boiled again. After cooling, 5 ml of the ammonia solution were added with continuous stirring, and the mixture was set aside for 5 min, heated gently and filtered into a 100-ml volumetric flask. The beaker, filter paper and precipitate were thoroughly washed with warm 3% sodium hydroxide solution. After cooling, 0.5 ml of the Triton X-100 solution was added and the solution was made up to volume with 3% sodium hydroxide solution.

*Preparation of the blank solution*

A second portion of the alloy, equal in weight to that taken for the preparation of the sample solution, was weighed into a 100-ml Pyrex glass beaker, 10 ml of distilled water and 5 ml of the sodium hydroxide solution were added, and after dissolution of the alloy, the mixture was boiled for 5 min and filtered into a second 100-ml Pyrex glass beaker. 15 ml of the saturated bromine water and 5 ml of the ammonium hydroxide solution were mixed in a third beaker and set aside for 5 min to ensure complete destruction of bromine. This mixture was added to the alloy filtrate, the solution heated (some iron may precipitate at this stage) and filtered into a 100-ml volumetric flask. After the addition of 0.5 ml of Triton X-100 solution, the solution was made up to volume with 3% sodium hydroxide solution.

*Recording of the polarograms and their quantitative interpretation*

The polarograms of the following solutions must be recorded:

1. the blank solution,
2. 50 ml of the sample solution pipetted into a dry, 100-ml beaker, and
3. the above solution (2), after the addition of 5 ml of the standard potassium dichromate solution.

Experimental conditions during recording must be kept constant, *i.e.* the same capillary, height of mercury column and galvanometer sensitivity must be employed for all three polarograms.

Temperature constancy must be ensured by the use of a suitable thermostat and oxygen removed by thorough de-aeration. The polarograms were recorded from  $-0.3$  V to  $-1.3$  V *vs.* S.C.E. Diffusion currents were measured by drawing a line connecting the peaks of the polarogram at  $-0.55$  V and  $-0.70$  V *vs.* S.C.E. and extrapolating it to  $-1.25$  V *vs.* S.C.E.; the distance from this point to the peak of the polarogram at the same potential was taken to represent the diffusion current. The chromium content of the alloy was calculated from the following formula:

$$\% \text{Cr} = \frac{(i_2 - i_1)}{(11(i_3 - i_1) - 10(i_2 - i_1))w}$$

where  $i_1$ ,  $i_2$  and  $i_3$  are the diffusion currents obtained by the above method from polaro-

grams of solutions 1, 2 and 3 respectively, and  $w$  is the weight of alloy in grams taken for the preparation of the sample and blank solutions.

## DISCUSSION

### *Preparation of the sample solution*

1. The dissolution of aluminum alloys in conc. sodium hydroxide solution is very convenient; in this medium, the choice of oxidizing agents available for the quantitative oxidation of chromium to the hexavalent state is rather restricted<sup>5-8</sup>. An alkaline bromine mixture was finally chosen because it ensured the formation of chromium(VI) from the outset, thus preventing the retention of chromium(III) in the hydroxide precipitate. Excess oxidizing agent must be removed quantitatively before the polarography; in the case of bromine, this was easily achieved by the addition of ammonia solution. The precipitate contains the hydroxides or oxides of iron, copper, manganese, nickel, etc.; chromium, zinc, aluminum and titanium pass into the filtrate. In the case of alloys containing lead, this also remains in the precipitate, because metallic lead does not dissolve in the medium used.

2. The accuracy of the results obtained by this method depends on the meticulous preparation of the blank solution containing the alloy and all the reagents used in the preparation of the sample solution, and differing from it only in the oxidation state of the chromium. Common reagent solutions must therefore be employed for the preparation of both sample and blank solutions and the volumes indicated in the procedure must be measured carefully.

3. The reagents must be introduced in the exact order given in the procedure to prevent the precipitation of chromic hydroxide; for that reason, bromine water must be added before the sodium hydroxide solution. The second portion of bromine water ensures the quantitative oxidation of the chromium.

4. Alloy samples containing considerable amounts of copper must be prepared by a slightly different method, owing to the appreciable solubility of cupric oxide in ammonia solution.

A preliminary filtration step, immediately after dissolution of the sample and before the addition of ammonia solution, prevents the passage of copper into the final sample solution. This filtration does not replace the filtration indicated in the procedure, which serves to remove traces of precipitate formed at this stage.

### *Preparation of the blank solution*

1. The procedure recommended for the preparation of the blank solution ensures its similarity to the sample solution in all respects except the oxidation state of the chromium. Distilled water replaces the initial bromine water, and a mixture of the appropriate volumes of bromine water and ammonia solution is added to the filtrate (this mixture must be previously prepared in a separate beaker, so that all the bromine is destroyed before its addition to the blank solution).

### *The polarographic determination*

The reduction of chromate ion in sodium hydroxide medium (0.1–1.0 *N*) gives rise to a well-defined polarographic wave, whose half-wave potential is  $-0.85$  V vs. S.C.E. The diffusion current is proportional to the concentration of chromate<sup>3</sup>. The residual

current cannot be deducted by the usual method of extrapolating the part of the polarographic curve preceding the wave to the potential at which it is desired to measure the diffusion current, because a polarogram of the supporting electrolyte alone also shows a small but distinct polarographic wave in this region. The diffusion current of this wave, which results mainly from the reduction of traces of iron present in the alkaline solution<sup>9</sup>, must be deducted from the diffusion current observed with chromate solutions. In the analysis of alloy samples, this blank diffusion current may be a considerable part of the measured chromate reduction diffusion current, and its exact determination is essential; hence, the sample solution and blank solution are prepared so that all factors, such as alkalinity, ionic strength, etc., are kept equal in both. Provided that this condition is fulfilled, the deduction of the blank diffusion current from that of the sample solution gives a diffusion current proportional to the chromium content of the sample.

2. The standard addition method was chosen as most appropriate for this determination, because the strongly alkaline medium in which the polarograms must be recorded necessitates the frequent replacement of capillaries, and because standard potassium dichromate solutions are easily prepared and stored.

TABLE I

Alloy No.	Weight of sample (w) g	$i_1$ mm*	$i_2$ mm	$i_3$ mm	Chromium	
					theor. %	found %
1	0.500	48	75	101	0.17	0.17
1	0.500	48	73	99	0.17	0.16
2	0.250	18.5	47.5	85.5	0.25	0.26
2	0.250	18.5	44.5	80.5	0.25	0.25
3	0.250	16	58	86	0.50	0.48
3	0.250	19	63	91.5	0.50	0.50
4	0.250	17.5	50	81	0.34	0.35
4	0.250	17.5	50	82	0.34	0.34

\* The diffusion currents  $i_1$ ,  $i_2$  and  $i_3$  are reported, as measured in the course of the analysis, in mm, there being no need of converting them into  $\mu\text{A}$  (only current ratios are involved in the calculation of results).

## RESULTS

The procedure was tested with aluminum alloys containing 0.1–0.5% chromium; various proportions of British Chemical Standards Alloy, No. 263, pure aluminum metal and standard potassium dichromate solution were mixed, and the synthetic alloys thus obtained were analyzed.

Table I shows some of the results obtained.

## SUMMARY

A convenient polarographic method for the determination of 0.1–0.5% of chromium in aluminum alloys is described. The alloy is dissolved in a bromine water–sodium hydroxide mixture; after suitable treatment, chromate is determined polarographically. Specific directions for the simultaneous running of a blank experiment are given; this provision greatly improves the accuracy of the results obtained.

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## RÉSUMÉ

Une méthode polarographique est proposée pour le dosage du chrome (0.1 à 0.5%) dans les alliages à base d'aluminium. Le chrome se trouve sous forme de chromate, après attaque de l'échantillon à analyser par l'eau de brome et l'hydroxyde de sodium.

## ZUSAMMENFASSUNG

Es wird eine polarographische Methode zur Bestimmung von Chrom (0.1–0.5%) in Aluminiumlegierungen beschrieben. Die Legierung wird in einem Gemisch von Natriumhydroxyd und Bromwasser gelöst und das entstandene Chromat polarographisch bestimmt.

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## STUDIES IN THE SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN MATERIALS DECOMPOSED BY HYDROFLUORIC ACID

### II. SPECTROPHOTOMETRIC DETERMINATION OF FLUOSILICIC ACID IN HYDROFLUORIC ACID

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## INTRODUCTION

Commercially hydrofluoric acid always contains small amounts of fluosilicic acid.

Earlier procedures for the determination of fluosilicic acid in the presence of hydrofluoric acid are based on unsatisfactory volumetric methods. KOLTHOFF<sup>1</sup> surveys the literature on this subject. He improves the volumetric method for the determination of both acids in mixture by evaporating the hydrofluoric acid in the presence of sodium chloride and hydrochloric acid. The remaining fluosilicate is titrated with standard alkali. The end-point is, however, not sharp, and the method requires large samples for the determination of low fluosilicic acid contents.

For the determination of small amounts of silicon photometric methods are more suitable. On the basis of investigations by CASE<sup>2</sup>, CADE<sup>3</sup> describes a procedure for the photometric determination of fluosilicic acid in commercial hydrofluoric acid. Most of the latter acid is separated by evaporation as recommended by KOLTHOFF. The

small amount of hydrofluoric acid remaining is converted to fluoboric acid, and the fluosilicic acid is determined photometrically as the yellow silicomolybdic acid.

In the present paper an improved method for the spectrophotometric determination of fluosilicic acid in hydrofluoric acid is described. The silicon is determined directly as  $\alpha$ -silicomolybdic acid without preceding evaporation of hydrofluoric acid.

#### *Instruments, reagents and apparatus*

Instruments, reagents and apparatus were the same as described in Part I of this series<sup>4</sup>, the only exception being the use of 2.000-cm glass cells.

#### *Experimental*

For the determination of the relatively small amounts of fluosilicic acid present in commercial hydrofluoric acid (normally below 0.25%), a special calibration curve was used in which the extinction of the  $\alpha$ -silicomolybdic acid was measured at a lower wavelength than usual. A wavelength of 370 m $\mu$  was suitable for amounts less than 1 mg SiO<sub>2</sub> per 100 ml.

A standard solution of silicic acid was prepared by decomposing 50.0 mg of silicon dioxide with 1.0 g of sodium carbonate, dissolving the melt in dilute hydrochloric acid and diluting to 500 ml; this solution contained 0.1 mg SiO<sub>2</sub> per ml.

Varying amounts of this standard solution were pipetted into plastic beakers containing about 50 ml of water. Ammonium molybdate (5 ml of 2% solution) was added and the pH adjusted to  $1.0 \pm 0.5$ . After 3 h on the boiling water bath the solutions were cooled to room temperature, transferred to 100-ml volumetric flasks and diluted to the mark. The extinction was measured at 370 m $\mu$  against a blank solution containing ammonium molybdate, adjusted to pH  $1.0 \pm 0.5$  and heated as the sample solution.

In Table I the extinction data and the extinction indexes ( $E/C$ ) are given for the series of solutions.

TABLE I

CALIBRATION CURVE FOR THE DETERMINATION OF FLUOSILICIC ACID IN HYDROFLUORIC ACID.  
WAVELENGTH 370 m $\mu$ . 2.000-cm CELLS

<i>Mg SiO<sub>2</sub> per 100 ml</i>	<i>Extinction</i>	<i>Extinction index (E/C)</i>
0.1	0.096	0.96
0.2	0.194	0.97
0.3	0.300	1.00
0.4	0.392	0.98
0.5	0.486	0.97
0.6	0.588	0.98
0.7	0.690	0.99
0.8	0.780	0.98

It is seen that Beer-Lambert's law is followed up to at least 0.8 mg SiO<sub>2</sub> per 100 ml.

### Procedure

From the hydrofluoric acid to be analyzed about 1 ml is transferred (with the teflon tube pipette or with a plastic measuring cylinder) to a weighed plastic beaker. The beaker is stoppered with a tightly fitting plastic stopper and reweighed. Then 50 ml of 25% aluminium chloride solution and 5 ml of 2% ammonium molybdate solution are added. The solution is diluted to about 90 ml with distilled water, the pH is adjusted to  $1.0 \pm 0.5$ , and the solution is heated, cooled and diluted as in the preparation of the calibration curve.

Finally the extinction is measured at 370 m $\mu$  and the content of fluosilicic acid calculated. A blank solution is prepared from the reagents and treated in the same way as the sample solution.

Analysis of commercial reagent grade hydrofluoric acid (35–40%) used in this investigation showed a content of 0.01% fluosilicic acid, which is well below the permitted maximum content of 0.25%.

### Complexing agents for hydrofluoric acid

Boric acid is frequently recommended to make hydrofluoric acid harmless by the formation of slightly dissociated fluoboric acid. At the start of the present investigations a saturated solution of boric acid in water was used to complex excess of hydrofluoric acid. It was, however, observed that the extinction of solutions of  $\alpha$ -silicomolybdic acid in volumetric flasks increased on standing, and it was concluded that this was due to attack on the glass.

The same phenomenon was not observed when aluminium chloride was used as complexing agent, and consequently this reagent was preferred.

### SUMMARY

A procedure is reported for the spectrophotometric determination of fluosilicic acid in commercial hydrofluoric acid. The determination of silicon as  $\alpha$ -silicomolybdic acid is carried out directly without previous separation of hydrofluoric acid.

### RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique de l'acide fluosilicique dans l'acide fluorhydrique commercial.

### ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Kieselfluorwasserstoffsäure in Fluorwasserstoffsäure handelsüblicher Qualität.

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# ÉTUDE DU COMPORTEMENT POLAROGRAPHIQUE DU ZIRCONIUM EN MILIEU ACIDE ET EN PRÉSENCE D'IONS NITRATE

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## INTRODUCTION

En étudiant le comportement polarographique des sels de zirconium en milieu chlorhydrique, LAUBENGAYER ET EATON<sup>1</sup> observent une onde de réduction ayant un potentiel de demi-onde voisin de  $-1,65$  V/E.C.S. et dépendant fortement de la concentration en ions hydrogène. Selon ces auteurs, cette onde serait la composante des ondes de réduction des ions hydrogène et zirconium. A pH 3, ils observent deux ondes distinctes; à des valeurs de pH supérieures à 4, l'une des ondes disparaît totalement.

Plus récemment, COZZI<sup>2</sup>, parvient à séparer les deux ondes aux pH inférieurs à 3, par addition de bleu de méthylène aux solutions.

Le but du présent travail consiste à étudier le comportement polarographique du zirconium en milieu acide et en présence d'ions nitrate. En effet, les ondes observées dans ce milieu présentent des caractéristiques susceptibles d'interprétation théorique et certaines applications analytiques.

## PARTIE EXPÉRIMENTALE

La liste des solutions étudiées figure au Tableau I. Le pH des solutions, contrôlé en cours de dilution à l'aide d'un pH mètre Radiometer 22, a été ajusté à l'aide de

TABLEAU I

[NaCl]	pH	[ZrO <sup>++</sup> ]
10 <sup>-1</sup> M	2	10 <sup>-3</sup> M
10 <sup>-1</sup> M	2	10 <sup>-5</sup> M
10 <sup>-1</sup> M	3	10 <sup>-3</sup> M
10 <sup>-1</sup> M	3	10 <sup>-5</sup> M
10 <sup>-1</sup> M	4	10 <sup>-3</sup> M
10 <sup>-1</sup> M	4	10 <sup>-4</sup> M
10 <sup>-1</sup> M	4	10 <sup>-5</sup> M

TABLEAU II

[H <sup>+</sup> ] en M/l	[ZrO <sup>++</sup> ]	I <sub>a</sub> en $\mu A$
10 <sup>-2</sup>	10 <sup>-3</sup>	150
10 <sup>-3</sup>	10 <sup>-3</sup>	15
10 <sup>-4</sup>	10 <sup>-3</sup>	3
10 <sup>-4</sup>	10 <sup>-4</sup>	0,35
10 <sup>-2</sup>	10 <sup>-5</sup>	125
10 <sup>-3</sup>	10 <sup>-5</sup>	10
10 <sup>-4</sup>	10 <sup>-5</sup>	pas d'onde
10 <sup>-2</sup>	10 <sup>-7</sup>	120

Les concentrations sont exprimées en moles/l;  
les courants de diffusion sont exprimés en  $\mu A$ .

solutions d'hydroxyde de sodium ou d'acide chlorhydrique calculées de manière à atteindre un volume final de 25 ml. Des quantités différentes de nitrate de sodium ont ensuite été ajoutées au moyen de micropipettes contrôlées.

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Les polarogrammes ont été tracés à l'aide d'un polarographe Radiometer PO<sub>4</sub>, à la température de 25.0° et avec un amortissement égal à 4. La constante capillaire n'a pas été déterminée, tous les polarogrammes ayant été pris dans les mêmes conditions avec le même capillaire.

### RÉSULTATS EXPÉRIMENTAUX

#### *Effet de la concentration en ions hydrogène et zirconium*

Les solutions ne contenant pas de nitrates ont d'abord été polarographiées. Le Tableau II indique les valeurs du courant de diffusion de l'onde obtenue à différentes concentrations en ions hydrogène et zirconium. Aucune onde n'a été observée aux pH 5 et 6, quelle que soit la concentration en ions zirconium, de même qu'à pH 4 pour des concentrations en ions zirconium égales à  $10^{-5}$  M. Des essais ont été effectués à pH 4 avec des solutions  $10^{-2}$  M en ions zirconium et 1 M en chlorure de sodium. A ce pH et cette force ionique, on obtient un précipité d'hydroxyde de zirconium.

Dans 3 milieux: pH 4  $[\text{ZrO}^{+2}] = 10^{-3}$  M, pH 2  $[\text{ZrO}^{+2}] = 10^{-5}$  M et pH 2  $[\text{ZrO}^{+2}] = 10^{-7}$  M, l'onde semble se diviser en deux ondes très voisines.

#### *Effet de la concentration en ions nitrate*

Une étude générale de l'effet de la teneur en ions nitrate a ensuite été réalisée en ajoutant respectivement aux 25 ml des solutions acides de zirconium préparées, 0.1 ml de diverses solutions de nitrate de sodium. Les conditions opératoires et les résultats

TABLEAU III

	[NO <sub>3</sub> -]							
	0	1·10 <sup>-7</sup>	1·10 <sup>-6</sup>	1·10 <sup>-5</sup>	1·10 <sup>-4</sup>	2·10 <sup>-4</sup>	1·10 <sup>-3</sup>	2·10 <sup>-3</sup>
<i>I<sub>a</sub></i> pH = 2 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-3}$ M	150 1.58	— —	150 1.60	150 1.63	3* 1.14	— —	30* 1.14	— —
<i>I<sub>a</sub></i> pH = 2 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-5}$ M	125 1.57	— —	125 1.57	125 1.57	125 1.57	— —	125 1.57	— —
<i>I<sub>a</sub></i> pH = 2 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-7}$ M	120 1.58	120 1.58	— —	120 1.58	120 1.57	— —	120 1.50	— —
<i>I<sub>a</sub></i> pH = 3 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-3}$ M	15 1.53	15 1.53	— —	0.4* 1.1	3* 1.1	6* 1.1	13* 1.1	— —
<i>I<sub>a</sub></i> pH = 3 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-5}$ M	10 1.54	10 1.54	— —	10 1.54	10 1.54	— —	10 1.54	— —
<i>I<sub>a</sub></i> pH = 4 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-3}$ M	3 1.52	— —	3 1.52	3 1.48	— —	— —	2* 1.0	— —
<i>I<sub>a</sub></i> pH = 4 <i>E<sub>1/2</sub></i> $[\text{ZrO}^{+2}] = 10^{-4}$ M	0.35 1.53	0.35 1.50	— —	0.35 1.48	— —	— —	0.35 1.34	0.35 1.32

obtenus sont groupés dans le Tableau III. Dans certaines conditions, on observe l'apparition d'une onde supplémentaire. La Fig. 1 montre 6 courbes polarographiques obtenues dans les conditions suivantes:

$[\text{ZrO}^{+2}] = 10^{-3} M$ ;  $\text{pH} = 2$ ;  $[\text{NaCl}] = 10^{-1} M$ ;  $[\text{NO}_3^-] = 1:0; 2:10^{-3} M; 3:2 \cdot 10^{-3} M; 4:3 \cdot 10^{-3} M; 5:4 \cdot 10^{-3} M; 6:6 \cdot 10^{-3} M$ .

Les courants de diffusion correspondant à l'apparition d'une onde de réduction due à la présence d'ions nitrate sont marqués d'une astérisque dans le Tableau III. On

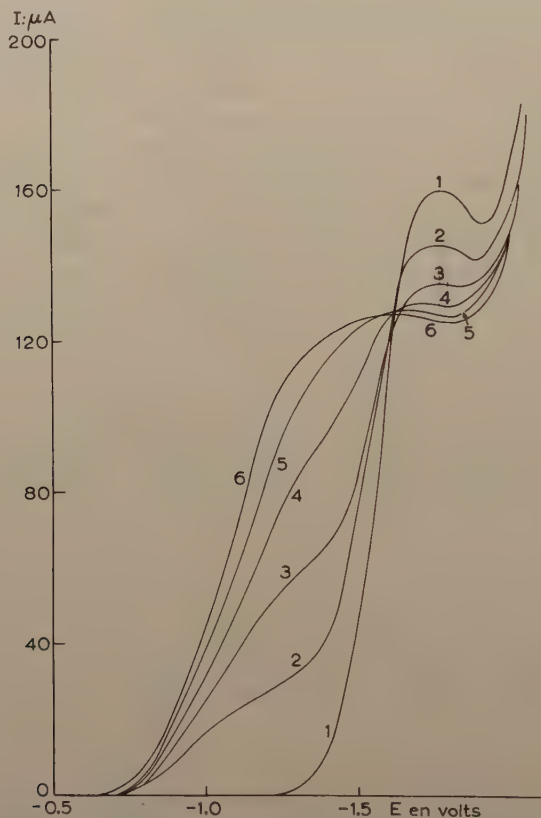


Fig. 1. Effet de la concentration en ions nitrate sur le courant de diffusion.

constate que la hauteur totale des deux ondes est dans tous les cas approximativement constante. L'ensemble des résultats obtenus montre l'existence aux  $\text{pH } 2,3$  et  $4$  d'une seconde onde de potentiel de demi-onde voisin de  $-1.00 \text{ V/E.C.S.}$  Sa hauteur dépend de la concentration en ions nitrate, mais n'est jamais supérieure à celle de l'onde due aux seuls ions hydrogène et zirconium.

L'effet de la teneur en ions nitrate pour le milieu  $10^{-3} M$  en ions zirconium à  $\text{pH } 2$  (Tableau IV) a ensuite été étudié de manière plus précise.

L'onde de potentiel de demi-onde voisin de  $-1.00 \text{ V/E.C.S.}$  est proportionnelle à la concentration en ions nitrate pour autant que la valeur du courant de diffusion soit inférieure à celle due aux ions hydrogène et zirconium.

Elle n'apparaît plus pour des concentrations en ions zirconium inférieures à  $10^{-5} M$ .

Nous avons d'autre part, étudié l'effet de la teneur en ions zirconium à concentration constante en ions nitrate et hydrogène. Le Tableau V montre, à pH 2 et pour une

TABLEAU IV

$[NO_3^-]$ en M/l	$I_{a_1}$	$E_{\frac{1}{2}}$	$I_a$ total	$E_{\frac{2}{2}}$
0	—	*	150	—1.62 V/E.C.S.
$1 \cdot 10^{-5}$	(0.5)	*	150	—1.62
$0.6 \cdot 10^{-4}$	1.7	*	150	—1.62
$1.1 \cdot 10^{-4}$	3.3	*	150	—1.62
$6.1 \cdot 10^{-4}$	18	*	140	—1.62
$1.11 \cdot 10^{-3}$	33	*	140	—1.60 V/E.C.S.
$1.0 \cdot 10^{-3}$	30	*	140	■
$2 \cdot 10^{-3}$	54	—1.20 V/E.C.S.	135	*
$4.5 \cdot 10^{-3}$	120	—1.30 V/E.C.S.	—	*
$7 \cdot 10^{-3}$	120	—1.20 V/E.C.S.	—	*
$1.7 \cdot 10^{-2}$	120	—1.12 V/E.C.S.	—	*
$3.7 \cdot 10^{-2}$	120	—1.05 V/E.C.S.	—	*
$7.7 \cdot 10^{-2}$	120	—1.02 V/E.C.S.	—	*

\* indique une onde trop irréversible pour pouvoir déterminer  $E_{\frac{1}{2}}$  avec précision.

concentration en ions nitrate égale à  $1 \cdot 10^{-3}$  M, la valeur du courant limite pour des concentrations en ions zirconium  $0.5 \cdot 10^{-3}$ ;  $1 \cdot 10^{-3}$ ;  $1.5 \cdot 10^{-3}$  et  $2 \cdot 10^{-3}$  M. Le courant limite de la première onde est indépendant de la teneur en ions zirconium.

TABLEAU V

$pH = 2$	$[NO_3^-] = 1 \cdot 10^{-3}$ M	
$[ZrO^{+2}]$	$I_{a_1}$	$I_a$ total
$0.5 \cdot 10^{-3}$	30	150
$1 \cdot 10^{-3}$	30	150
$1.5 \cdot 10^{-3}$	30	150
$2 \cdot 10^{-3}$	30	150

TABLEAU VI

$[ZrO^{+2}] = 10^{-3}$ M.		$[NO_3^-] = 1 \cdot 10^{-4}$ M.	
$pH$	$[H^+]$	$I_{a_1}$	$I_{a_2}$
2.77	$1.70 \cdot 10^{-3}$	3	22
2.52	$3 \cdot 10^{-3}$	3	36
2.17	$6.7 \cdot 10^{-3}$	3	74
1.86	$1.4 \cdot 10^{-2}$	3	144

Enfin, les résultats groupés dans le Tableau VI montrent que si la concentration en ions nitrate vaut  $10^{-4}$  M et la concentration en ions zirconium  $10^{-3}$  M, le courant limite de diffusion est indépendant du pH, aux pH 2.77; 2.52; 2.17 et 1.86.

#### EFFET DE LA TEMPÉRATURE ET DE LA PRESSION DE LA COLONNE DE MERCURE

L'effet de la température et de la hauteur de la colonne de mercure sur le courant de diffusion est résumé dans les Tableaux VII et VIII.

#### DISCUSSION

L'ensemble de nos résultats expérimentaux montre qu'en milieu acide et en présence d'ions zirconium, les ions nitrate se réduisent à l'électrode à goutte de mercure. Le potentiel de demi-onde correspondant à cette réduction catalysée est voisin de —1.00

V/E.C.S.; la hauteur de l'onde polarographique n'est pas proportionnelle à la racine carrée de la hauteur du réservoir de mercure (Tableau VII) mais le courant de diffusion dépend de la température de la même manière qu'une onde de diffusion normale (Tableau VIII), soit environ 2.5 % par degré centigrade.

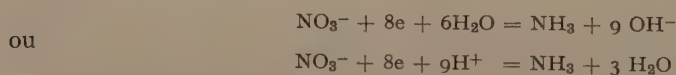
TABLEAU VII

Solution	$h_1 = 70 \text{ cm}$ $\sqrt{h} = 8.37$		$h_2 = 55 \text{ cm}$ $\sqrt{h} = 7.42$		$h_3 = 40 \text{ cm}$ $\sqrt{h} = 6.33$	
	$I_{a_1}$	$I_{a_2}$	$I_{a_1}$	$I_{a_2}$	$I_{a_1}$	$I_{a_2}$
pH = 2 [ZrO <sup>+2</sup> ] = 10 <sup>-3</sup> M	33	150	31	140	30	120
pH = 3 [ZrO <sup>+2</sup> ] = 10 <sup>-3</sup> M	—	17	—	16	—	14
pH = 2 [ZrO <sup>+2</sup> ] = 10 <sup>-5</sup> M	—	150	—	140	—	130

TABLEAU VIII

Solution	$T = 25^\circ$		$T = 35^\circ$	
	$I_{a_1}$	$I_{a_2}$	$I_{a_1}$	$I_{a_2}$
pH = 2 [ZrO <sup>+2</sup> ] = 10 <sup>-3</sup> M [NO <sub>3</sub> <sup>-</sup> ] = 1.11 · 10 <sup>-3</sup> M	31	110	42	120

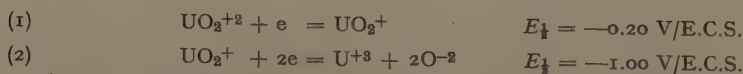
On peut rapprocher le comportement polarographique des ions nitrate en présence d'ions zirconium à celui observé pour les ions nitrate dans une solution d'ions polyvalents<sup>3-5</sup> tels que les ions uranium. Le schéma proposé pour cette réduction est généralement le suivant:



La réduction des nitrates à l'électrode consommant des ions H<sup>+</sup>, la hauteur de l'onde des nitrates ne peut dépasser une certaine valeur, fonction de la concentration en ions H<sup>+</sup> et UO<sub>2</sub><sup>+</sup> ou ZrO<sup>+2</sup>. En effet, la quantité d'ions H<sup>+</sup> diminuant le pH s'élève et les ions UO<sub>2</sub><sup>+</sup> ou ZrO<sup>+2</sup> précipitent.

Dans le cas de l'uranium on observe une onde de réduction des ions nitrate à —1.00 V/E.C.S., située exactement au même potentiel que la seconde onde de réduction du cation uranyle.

On a en effet:



La réduction des nitrates serait donc catalysée par le cation UO<sub>2</sub><sup>+</sup> ou U<sup>+5</sup>.

Pour le zirconium, ce serait le cation ZrO<sup>+2</sup> ou Zr<sup>+4</sup> qui catalyserait la réaction.

La charge des cations  $U^{+5}$  et  $Zr^{+4}$  étant plus importante que celle des cations  $UO_2^+$  et  $ZrO^{+2}$ , on peut faire l'hypothèse que ce sont effectivement eux, qui à l'électrode,

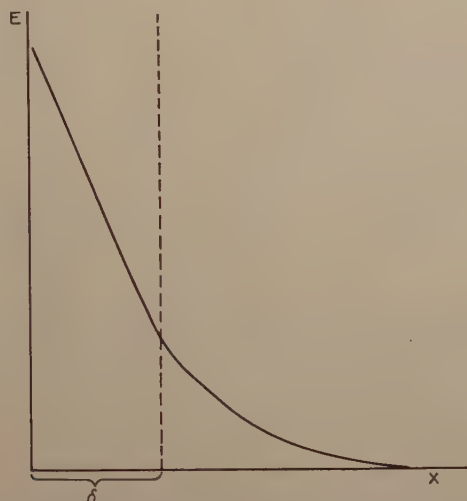


Fig. 2. Distribution du potentiel dans la double couche ionique.

jouent le rôle de catalyseur. En effet, on peut montrer que la concentration à une distance  $\delta$  de la surface de l'électrode correspondant au centre de gravité des charges attirées par l'électrode (plan  $\delta$ ) peut être beaucoup plus grande en cations fortement chargé, qu'au sein de la solution. Dans le cas du zirconium, si la distribution du dépolarisant reste boltzmannienne jusqu'au plan  $\delta$ , ce rapport serait donné par :

$$\log \frac{(Zr^{+4})\delta}{(Zr^{+4}) \text{ sol}} = \frac{-1}{2.31} \frac{ZF}{RT} \psi = \frac{-4}{0.059} \psi = \frac{-4}{0.059} (-10^{-1}) \approx 8$$

D'où :

$$\frac{(Zr^{+4})\delta}{(Zr^{+4}) \text{ sol}} \approx 10^8$$

où  $\psi$ , de l'ordre de  $-10^{-1}$ , est le potentiel relatif à une distance  $\delta$  de l'électrode. Le potentiel  $\psi$  peut être calculé en fonction de la charge de l'électrode. Les détails de ces calculs sont décrits par L. GIERST<sup>6</sup>.

Si la réaction  $ZrO^{+2} + 2 H^+ = Zr^{+4} + H_2O$  peut se produire, il peut y avoir accumulations d'ions  $Zr^{+4}$  à l'électrode. Le cation  $Zr^{+4}$  formé pourrait alors, à l'électrode, catalyser la réduction des nitrates. Nous avons vérifié expérimentalement cette hypothèse à l'aide des solutions suivantes (Fig. 3) :

1) Sol.  $2 \cdot 10^{-3} M$  en  $ZrO^{+2}$ ,  $2 \cdot 10^{-2} M$  en  $H^+$ ,  $2 \cdot 10^{-3} M$  en  $NO_3^-$ ,  $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1} M$ .

2) Sol.  $2 \cdot 10^{-3} M$  en  $ZrO^{+2}$ ,  $10^{-2} M$  en  $H^+$ ,  $2 \cdot 10^{-3} M$  en  $NO_3^-$ ,  $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1} M$ .

3) Sol.  $10^{-3} M$  en  $ZrO^{+2}$  et  $2 \cdot 10^{-2} M$  en  $H^+$ ,  $2 \cdot 10^{-3} M$  en  $NO_3^-$ ,  $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1} M$ .

4) Sol.  $10^{-3} M$  en  $ZrO^{+2}$  et  $4 \cdot 10^{-2} M$  en  $H^+$ ,  $2 \cdot 10^{-3} M$  en  $NO_3^-$ ,  $(H^+) + (Na^+) = C^{te} = 1,1 \cdot 10^{-1} M$ .

5) Sol.  $10^{-3} M$  en  $ZrO^{+2}$  et  $8 \cdot 10^{-2} M$  en  $H^+$ ,  $2 \cdot 10^{-3} M$  en  $NO_3^-$ ,  $(H^+) + (Na^+) = C^{te} = 1,1 \cdot 10^{-1} M$ .

On observe que la courbe correspondant à la solution 4 correspond parfaitement avec celle de la solution 2.

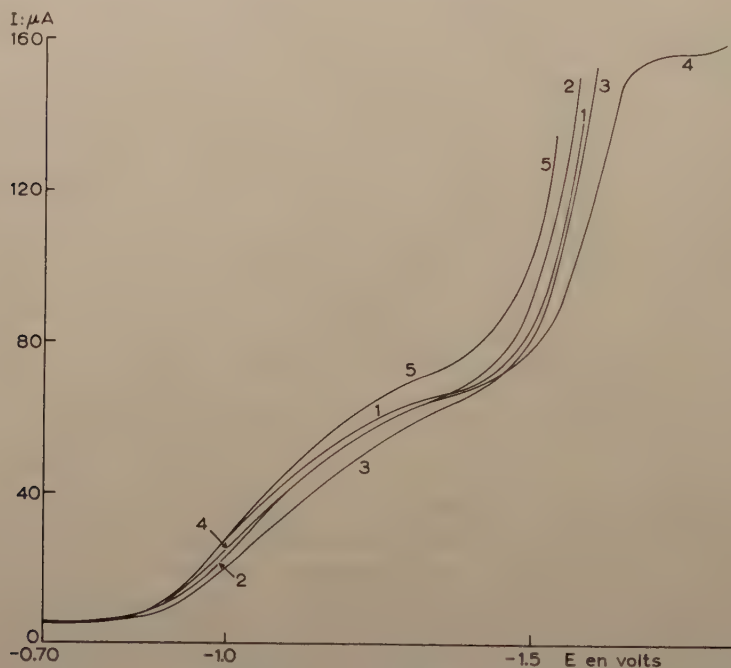


Fig. 3. Effet de la concentration en ions hydrogène sur le courant de diffusion.

Par contre, la solution 3 donne une onde située en dessous de celle de la solution 2, tandis que la solution 5 donne une onde située au-dessus.

On voit donc, en examinant les ondes polarographiques obtenues, que la réduction des nitrates s'opère à l'aide d'un mécanisme d'ordre deux en  $H^+$  par rapport au zirconium.

Ceci confirme donc l'hypothèse que l'accumulation des ions  $Zr^{+4}$  se produit effectivement à l'électrode et que ce sont vraisemblablement les ions  $Zr^{+4}$  et non  $ZrO^{+2}$  qui catalysent la réduction des ions nitrates.

#### CONCLUSION

La réduction des nitrates à l'électrode à goutte est catalysée par les ions  $Zr^{+4}$  produits en milieu acide selon la réaction  $ZrO^{+2} + 2 H^+ = Zr^{+4} + H_2O$  et accumulés à l'électrode. Cette hypothèse a été vérifiée expérimentalement. L'onde de réduction obtenue peut servir au dosage quantitatif des ions nitrate lorsque leur concentration varie entre  $1 \cdot 10^{-5}$  et  $5 \cdot 10^{-3} M$  à pH 2 si la teneur en ions zirconyle est voisine de  $10^{-3} M$ .

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## REMERCIEMENTS

Nous tenons à remercier M. L. GIERST, chef de travaux à l'Université de Bruxelles des suggestions qu'il nous a données pour l'interprétation de nos résultats.

## RÉSUMÉ

On observe, en présence de zirconium, une onde de réduction catalytique des ions nitrate, à l'électrode à goutte de mercure. Cette onde peut servir au dosage quantitatif des ions nitrate. On donne, en outre, le mécanisme du processus de réduction.

## SUMMARY

In the presence of zirconium, one observes a catalytic reduction wave of nitrate ions at the mercury dropping electrode. This wave can be used for the quantitative determination of nitrate ions. The mechanism of the reduction is explained.

## ZUSAMMENFASSUNG

In Gegenwart von Zirkonium geben Nitrat-Ionen an der Quecksilbertropfenelektrode eine Welle, die eine katalytische Reduktion anzeigt. Diese Welle kann zur quantitativen Bestimmung von Nitrat-Ionen verwendet werden. Eine Erklärung für den Mechanismus der Reduktion ist gegeben.

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## THE CHARACTERIZATION AND IDENTIFICATION OF THE RARE-EARTH CHLORIDE HYDRATES BY DIFFERENTIAL THERMAL ANALYSIS

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Although there are a number of techniques that can be used to identify the rare-earth elements, a simple and convenient method, differential thermal analysis (DTA), has long been neglected. By this method, the qualitative identification of a rare-earth compound is possible by determining the temperatures at which exothermic (exotherms) or endothermic (endotherms) reactions take place as the substance is heated<sup>1</sup>. Under similar conditions of sample size and packing, furnace heating rate, and type of recorder, these exotherm and endotherm temperature maximas are reproducible enough so as to be useful for the identification of a series of rare-earth compounds. This method is valuable for the identification of the individual rare-earths or, in certain cases, for mixtures of them.

For our first investigation, the thermal decomposition of all of the rare-earth chloride hydrates (except Pm) were studied by DTA. The metal chlorides were in the form of the 6- or 7-hydrates and were the same compounds that had previously been studied on the thermobalance<sup>2,3</sup>.

## EXPERIMENTAL

### Reagents

The rare-earth compounds were obtained in the form of their oxides of 99.9% purity from Research Chemicals, Inc., Burbank, Calif., and the Lindsay Chemical Co., West Chicago, Ill. The purity was that listed by the supplier.

### Preparation of salts

The rare-earth chloride hydrates were prepared as previously described<sup>1</sup>.

### DTA apparatus

The apparatus consisted of a stainless steel sample holder and furnace; a motor-driven variable transformer to control the furnace heating rate; and a strip-chart microvolt recorder<sup>4</sup>. The differential temperatures were measured with 28 gauge platinum—90% platinum—10% rhodium thermocouples. Sample sizes ranged in weight from 0.200 to 0.215 g and were mixed with ignited alumina in a 1:1 ratio; ignited alumina was also used in the reference chamber. The furnace heating rate was about 10.5° per min. Thermograms were recorded on 5 in. wide chart paper using a chart speed of 6 in. per h.

## DISCUSSION

The thermograms of the rare-earth chloride hydrates are given in Figs. 1–3. The prominent endotherm maxima temperatures are given in Table I.

On the basis of the thermograms, it is convenient, for purposes of discussion, to classify the thermal decomposition patterns into 4 main groups: Group I—La, Ce, Pr, and Nd; Group II—Sm, Eu, and Gd; Group III—Tb, Dy, Y, Ho, Er, and Tm; Group IV—Yb and Lu. These groups are just arbitrary but unpublished results on the thermal decomposition of the rare-earth nitrate hydrates reveal much the same classification.

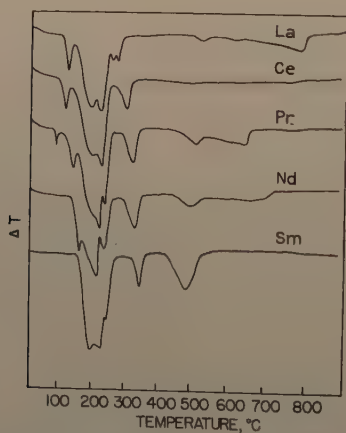


Fig. 1. Thermograms of the rare-earth chloride hydrates. Lanthanum to samarium.

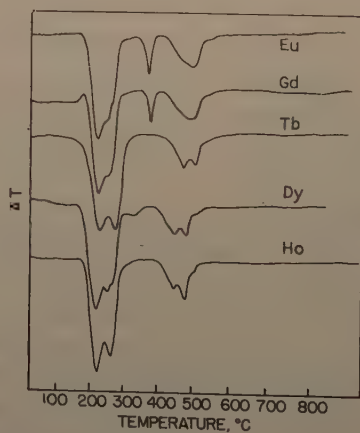


Fig. 2. Thermograms of the rare-earth chloride hydrates. Europium to holmium.

Group I

In this group, the thermograms are characterized by one or two small endotherms which precede the large dehydration endotherms. These small endotherms are thought to arise from the heat absorbed by the partial fusion of the metal salts. Also observed in this group, with the exception of cerium, are the endotherms in the 400°-650°

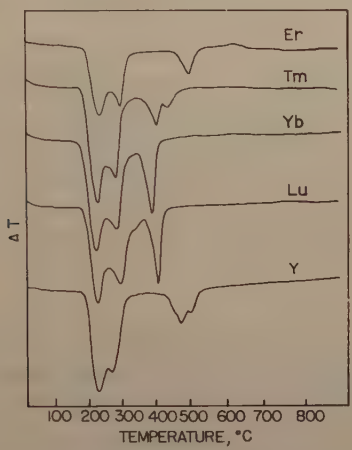


Fig. 3. Thermograms of the rare-earth chloride hydrates. Erbium to yttrium.

temperature range. It is known from thermobalance studies<sup>1</sup> that the terminal thermal decomposition products are the metal oxychlorides and these endotherms are presumed to be due to their formation. As the atomic weight of the rare-earth metal ion increased, the metal oxychlorides were obtained at progressively lower temperatures; this could explain the disappearance of these endotherms in the other groups studied.

TABLE I

MAXIMA TEMPERATURES FOR THE ENDOTHERMS OF THE RARE-EARTH CHLORIDE HYDRATES

Rare-earth salt	Temperature, °C					
LaCl <sub>3</sub> .7H <sub>2</sub> O	110	163	190	215	430	650
CeCl <sub>3</sub> .6H <sub>2</sub> O	100	170	185	250		
PrCl <sub>3</sub> .7H <sub>2</sub> O	75	120	180	190	260	410
NdCl <sub>3</sub> .6H <sub>2</sub> O	135	175	190	270	400	525
SmCl <sub>3</sub> .6H <sub>2</sub> O	160	190	275	390		
EuCl <sub>3</sub> .6H <sub>2</sub> O	180	295	400			
GdCl <sub>3</sub> .6H <sub>2</sub> O	180	300	390			
TbCl <sub>3</sub> .6H <sub>2</sub> O	180	220	380	405		
DyCl <sub>3</sub> .6H <sub>2</sub> O	175	205	355	385		
HoCl <sub>3</sub> .6H <sub>2</sub> O	175	210	350	380		
ErCl <sub>3</sub> .6H <sub>2</sub> O	190	240	400			
TmCl <sub>3</sub> .6H <sub>2</sub> O	180	255	320	350		
YbCl <sub>3</sub> .6H <sub>2</sub> O	180	227	310			
LuCl <sub>3</sub> .6H <sub>2</sub> O	180	235	325			
YCl <sub>3</sub> .6H <sub>2</sub> O	185	220	380			

### Group II

In this group, the large dehydration endotherms consisted entirely of just one maxima with several small endotherm shoulders. There were sharp endotherms in the  $160^{\circ}$ – $180^{\circ}$  temperature range and broad endotherms in the  $390^{\circ}$ – $400^{\circ}$  temperature range. The latter are presumed to be due to the formation of the metal oxychlorides; thermobalance studies appear to confirm this.

### Group III

By far the largest group, this group is characterized by the splitting of the dehydration endotherms into two maximas and also the splitting of the oxychloride formation endotherms. The splitting of the former resulted in the formation of maximas in the  $175^{\circ}$ – $190^{\circ}$  and the  $205^{\circ}$ – $240^{\circ}$  temperature range. It is interesting to observe that the thermogram for yttrium appears to fit nicely between dysprosium and holmium, in agreement with results found from separation studies<sup>5</sup>.

### Group IV

In this group, the splitting of the dehydration endotherms were again observed but new endotherms appeared in the  $310^{\circ}$ – $325^{\circ}$  temperature range. These new endotherms were characterized by their rather sharp, narrow appearance; in contrast to the broad endotherms found in this region in the Group III compounds.

### SUMMARY

The thermal decomposition of all of the rare-earth chloride hydrates was studied by differential thermal analysis. By use of the resulting thermograms, it is possible to apply this method as a means of identification of the individual rare-earth elements. The endotherm temperature maximas are recorded and discussed for all of the rare-earth compounds.

### RÉSUMÉ

Une étude sur la décomposition thermique des chlorures de terres rares hydratés a été effectuée par l'analyse thermique différentielle. Les thermogrammes obtenus peuvent être utilisés pour l'identification de ces éléments.

### ZUSAMMENFASSUNG

Die thermische Zersetzung der Chlorid-Hydrate aller seltenen Erden wurden mit Hilfe differential-thermoanalytischer Methoden untersucht. Die erhaltenen Thermogramme ermöglichen die Identifizierung der einzelnen seltenen Erden.

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THE CONDUCTOMETRIC TITRATION OF CARBOXYLIC AND  
PHENOLIC ACIDS IN NON-AQUEOUS SOLUTIONSIII. THE RESOLUTION OF ACID MIXTURES AND SOME PRACTICAL  
APPLICATIONS

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## INTRODUCTION

During preliminary investigations on the conductometric determination of acids<sup>1</sup> it was observed that when certain dibasic compounds were titrated in pyridine or dimethylformamide (DMF) with a quaternary ammonium base, an N-shaped titration curve with two distinct equivalence points was obtained. Other dibasic acids gave, under the same conditions, a chair-shaped curve with less distinct end-points. The titration of monobasic acids was the least satisfactory; in general only slight breaks were observed in the conductance curves.

From the results described previously<sup>1</sup> and also from the high-frequency titrations under similar conditions described by ISHIDATE AND MASUI<sup>2</sup>, it was expected that suitable mixtures of acids could be resolved by conductometric titration, especially those consisting of a monobasic acid and a dibasic acid giving an N-shaped curve. In addition it should be possible to resolve some binary mixtures of dibasic acids.

From the foregoing it is clear that the results are primarily determined by the accuracy with which the dibasic acids can be titrated. The optimum conditions for these acids were studied in the second paper of this series<sup>3</sup>, the strong influence of solvent and base being discussed. The best results were obtained in media of low solvating power, *e.g.* pyridine, DMF and, to a less extent, propanol-2 and methanol-benzene mixtures. A low dielectric constant, *i.e.* below 20, also improved the results, although under these circumstances complications arose owing to the strongly decreasing conductance of the solutions<sup>3</sup>. As to the bases used, it was found that titration of dibasic acids could be carried out with titrants derived from small cations ( $K^+$ ,  $(CH_3)_4N^+$ ) and with amines in solvents containing alcohol, or better, with tetrabutylammonium hydroxide in DMF or pyridine.

The titrations described in the present paper were mainly done under the optimum conditions found in the preceding investigations and the present results pertain only to these conditions. In the same way we have restricted ourselves to titrations at room temperature, although higher temperatures might be favourable<sup>3</sup>. In spite of these limitations, the investigation gives an idea of the possibilities of conductometric titration of acid mixtures in non-aqueous media.

## EXPERIMENTAL

*Titants and solvents*

The bases used were potassium methoxide in pyridine-benzene, and tetramethyl- and tetrabutylammonium hydroxide in methanol-benzene. For the preparation of these titants, see the first paper of this series<sup>1</sup>. The strength of the bases varied between 0.1 and 0.3 *N*.

The solvents used were methanol, pyridine and dimethylformamide. In addition, mixtures of one or two of these solvents with benzene or xylene were sometimes applied. All the solvents were of reagent grade and contained only minor quantities of water (0.1–0.5%).

*Electrical equipment*

The resistance measurements were carried out with the same instruments as previously described<sup>1,3</sup>. A relative accuracy of  $\pm 0.5\%$  proved to be sufficient for our purpose.

*Titration procedure*

The acid mixtures were weighed accurately in 5-ml beakers (tall form) in such quantities that 1–2 ml of base was required per acid group to be determined. Then the volume was made up to 25–50 ml, the electrode assembly inserted and the magnetic stirrer started. The titrant was added by means of a 10-ml burette in 0.1-ml portions, the equilibrium reading of the bridge being taken after each addition.

## DISCUSSION OF RESULTS

*1. Binary mixtures of carboxylic acids*

The following binary mixtures of carboxylic acids were titrated:

a. a mono- and a dibasic acid in methanol (Table I), b. a mono- and a dibasic acid in dimethylformamide (Table II), c. a mono- and a dibasic acid in pyridine or DMF-benzene (1:3 v/v) (Table III), d. two dibasic acids in non-solvating media (Table IV).

*a. A mono- and a dibasic acid in methanol*

From the results given in Table I it can be seen that in principle resolution is possible for those mixtures in which the dibasic acid has a high  $K_1/K_2$  ratio<sup>3</sup> in water.

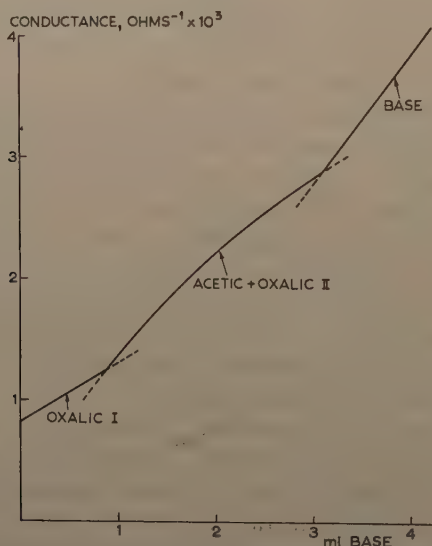


Fig. 1. Titration of a mixture of acetic acid and oxalic acid in methanol with tetramethylammonium hydroxide.

Hence, only oxalic, malonic, maleic and phthalic acid can be determined in methanol in the presence of a monobasic acid. However, the accuracy with which the end-points can be estimated in this solvent is not high (dibasic acids give only chair-shaped curves in methanol), as shown in Fig. 1. In this example the first equivalence point corresponds to the neutralization of one carboxyl group of the oxalic acid and the second to that of the other carboxyl group of the dibasic acid plus the monobasic acid. In general, the sequence of the titration is first the monobasic acid plus one function of the dibasic acid, followed by the second function of the dibasic compound.

TABLE I

TITRATION OF A MONO- AND A DIBASIC ACID IN METHANOL

Monobasic compound	Dibasic compound	Base	Number of equivalence points	Resolution possible (+) or impossible (-)
acetic acid	oxalic acid	Me <sub>4</sub> NOH <sup>a</sup>	2	+
acetic acid	malonic acid	Me <sub>4</sub> NOH	2	+
acetic acid	fumaric acid	Me <sub>4</sub> NOH	1	—
acetic acid	maleic acid	Me <sub>4</sub> NOH	3	+
acetic acid	tartaric acid	Me <sub>4</sub> NOH	1	—
benzoic acid	oxalic acid	Me <sub>4</sub> NOH	2	+
benzoic acid	malonic acid	Me <sub>4</sub> NOH	2	+
benzoic acid	succinic acid	Me <sub>4</sub> NOH	1	—
benzoic acid	tartaric acid	Me <sub>4</sub> NOH	1	—
benzoic acid	phthalic acid	Me <sub>4</sub> NOH	2	+
benzoic acid	isophthalic acid	Me <sub>4</sub> NOH	1	—
salicylic acid	oxalic acid	Me <sub>4</sub> NOH	2	+
salicylic acid	tartaric acid	Ne <sub>4</sub> NOH	1	—
salicylic acid	phthalic acid	Me <sub>4</sub> NOH	2	+
salicylic acid	isophthalic acid	Me <sub>4</sub> NOH	1	—

<sup>a</sup> Me<sub>4</sub>NOH = tetramethylammonium hydroxide

#### b. A mono- and a dibasic acid in DMF

In DMF the titration curve of dibasic acids has a more pronounced chair shape than in methanol and in some cases even N-shapes may be obtained (maleic and phthalic acid). Thus the accuracy of the titrations is better in DMF than in methanol, and the possibilities of resolving a binary mixture are greater. This follows from a comparison of the results given in Tables I and II. For instance, a mixture of salicylic and isophthalic acids can be resolved in DMF, but not in methanol.

As a consequence of the low solvating power of DMF, precipitate formation may be expected in some cases (*e.g.* with oxalic and fumaric acid) when bases with small cations are used. In general, precipitate formation does not affect the accuracy of the end-point, but the time required for a titration usually increases because of the rather slow precipitation in non-aqueous media.

Fig. 2 shows the titration curve of an acid mixture in DMF. It is clear that the end-points can be determined with greater accuracy than in Fig. 1. The first equivalence point corresponds to the neutralization of the caproic acid plus one function of the succinic acid and the second function of the dibasic acid is titrated between the first and the second end-points.

TABLE II

TITRATION OF A MONO- AND A DIBASIC ACID IN DIMETHYLFORMAMIDE

Monobasic compound	Dibasic compound	Base	Number of equivalence points	Resolution possible(+) or impossible(-)	Remarks
acetic acid	oxalic acid	Me <sub>4</sub> NOH	1	—	precipitate
acetic acid	malonic acid	Me <sub>4</sub> NOH	2	+	
acetic acid	succinic acid	Me <sub>4</sub> NOH	2	+	
acetic acid	fumaric acid	Me <sub>4</sub> NOH	—	—	precipitate
acetic acid	maleic acid	Me <sub>4</sub> NOH	2	+	
acetic acid	tartaric acid	Me <sub>4</sub> NOH	1	—	
caproic acid	succinic acid	Me <sub>4</sub> NOH	2	+	
benzoic acid	oxalic acid	Me <sub>4</sub> NOH	2	+	precipitate
benzoic acid	malonic acid	Me <sub>4</sub> NOH	3	+	
benzoic acid	succinic acid	Me <sub>4</sub> NOH	2	+	
benzoic acid	tartaric acid	Me <sub>4</sub> NOH	1	—	
benzoic acid	phthalic acid	Me <sub>4</sub> NOH	3	+	
benzoic acid	isophthalic acid	Me <sub>4</sub> NOH	1	—	
salicylic acid	oxalic acid	Me <sub>4</sub> NOH	2	+	precipitate
salicylic acid	tartaric acid	Me <sub>4</sub> NOH	2	+	
salicylic acid	phthalic acid	Me <sub>4</sub> NOH	2	+	
salicylic acid	isophthalic acid	Me <sub>4</sub> NOH	2	+	

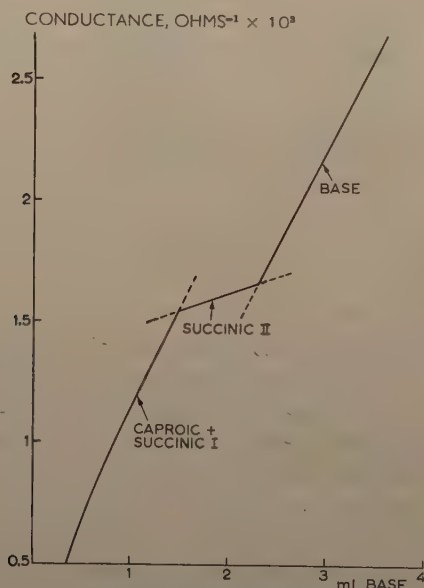


Fig. 2. Titration of a mixture of caproic acid and succinic acid in DMF with tetramethylammonium hydroxide.

*c. A mono- and a dibasic acid in pyridine or DMF-benzene (1:3 v/v)*

Most of the titrations were carried out in pyridine or in a DMF-benzene mixture (1:3 v/v); these have the same dielectric constant and solvating power. With a few exceptions resolution of suitable mixtures is possible by means of both tetramethyl-

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ammonium hydroxide and tetrabutylammonium hydroxide. The former base generally gives insoluble neutral tetramethylammonium salts of dibasic acids, but, as in the case of pure DMF, this does not affect the analytical results.

Figures 3 and 4 give examples of resolving titrations in pyridine. In most cases the monobasic acid and the first acidic proton of the dibasic acid are titrated together (Fig. 3), but three equivalence points may also be found (Fig. 4). In this case the first and third end-point correspond to the neutralization of the dibasic compound and the second to that of the monobasic acid (see also under d). (Salicylic acid, when titrated with a quaternary ammonium base, behaves as a monobasic acid; see also under 2).

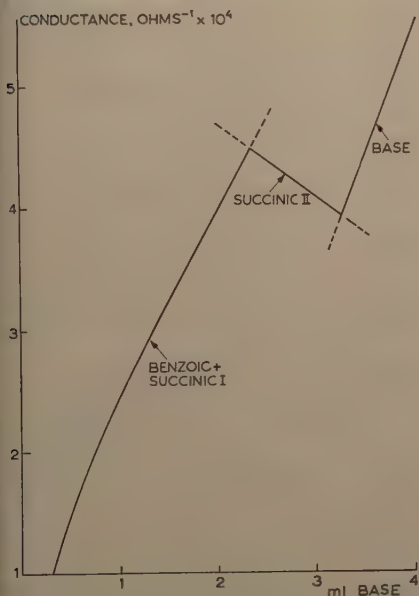


Fig. 3. Titration of a mixture of benzoic acid and succinic acid in pyridine with tetrabutylammonium hydroxide.

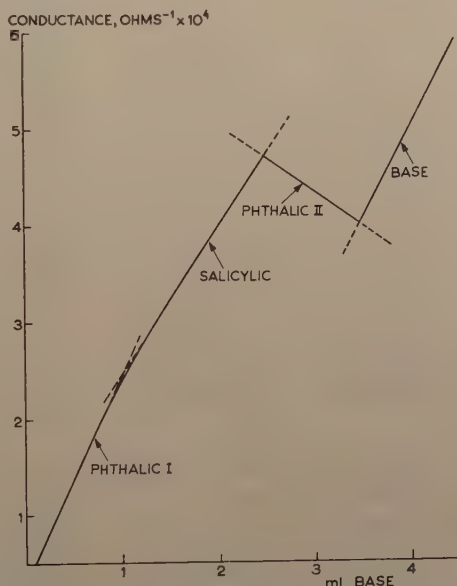


Fig. 4. Titration of a mixture of salicylic acid and phthalic acid in pyridine with tetrabutylammonium hydroxide.

When the data given in Table III are compared with those in Tables I and II, it is clear that pyridine and DMF-benzene mixtures are to be preferred for the conductometric titration of mixtures of organic acids, especially when tetrabutylammonium hydroxide is used as the base (*cf.* the results obtained by VAN DER HEIJDE<sup>4</sup> in potentiometric titrations of organic acids and those obtained by CUNDIFF AND MARKUNAS<sup>5</sup> for mixtures of strong inorganic acids).

In the resolution of acid mixtures in non-solvating media of low dielectric constant, better results can sometimes be obtained when other solvent compositions are used instead of those mentioned above. Thus, mixtures of pyridine and DMF or of pyridine and benzene are in some cases to be preferred (*cf.* resolution of benzoic-isophthalic acid and benzoic-terephthalic acid, Table III).

It should be borne in mind that the limiting ratio of the two compounds in a mixture that can be resolved conductometrically is the same as for potentiometric

TABLE III

TITRATION OF A MONO- AND A DIBASIC ACID IN PYRIDINE OR DMF-BENZENE(XYLENE) (1:3 v/v)

Monobasic compound	Dibasic compound	Base	Number of equivalence points	Resolution possible(+) or impossible(-)	Remarks
acetic acid	oxalic acid	Me <sub>4</sub> NOH	1	—	precipitate
acetic acid	oxalic acid	Bu <sub>4</sub> NOH <sup>a</sup>	2	+	
acetic acid	malonic acid	Me <sub>4</sub> NOH	3	+	precipitate
acetic acid	malonic acid	Bu <sub>4</sub> NOH	3	+	
acetic acid	succinic acid	Me <sub>4</sub> NOH	—	—	precipitate
acetic acid	fumaric acid	Me <sub>4</sub> NOH	1	—	
acetic acid	maleic acid	Me <sub>4</sub> NOH	3	+	precipitate
acetic acid	maleic acid	Bu <sub>4</sub> NOH	2	+	
acetic acid	tartaric acid	Bu <sub>4</sub> NOH	2	+	
caproic acid	succinic acid	Me <sub>4</sub> NOH	—	—	precipitate
benzoic acid	oxalic acid	Bu <sub>4</sub> NOH	3	+	
benzoic acid	malonic acid	Me <sub>4</sub> NOH	3	+	precipitate
benzoic acid	malonic acid	Bu <sub>4</sub> NOH	3	+	
benzoic acid	succinic and	Me <sub>4</sub> NOH	2	+	precipitate
benzoic acid	succinic acid	Bu <sub>4</sub> NOH	2	+	
benzoic acid	tartaric acid	Bu <sub>4</sub> NOH	1	—	
benzoic acid	phthalic acid	Me <sub>4</sub> NOH	3	+	precipitate
benzoic acid	phthalic acid	Bu <sub>4</sub> NOH	3	+	
benzoic acid	isophthalic acid	Me <sub>4</sub> NOH	2	+	pyr.-DMF (4:1 v/v)
benzoic acid	isophthalic acid	Bu <sub>4</sub> NOH	1	—	
benzoic acid	terephthalic acid	Me <sub>4</sub> NOH	—	—	precipitate
benzoic acid	terephthalic acid	Me <sub>4</sub> NOH	2	+	precipitate (pyr.-benzene (4:1 v/v))
benzoic acid	terephthalic acid	Bu <sub>4</sub> NOH	1	—	
salicylic acid	oxalic acid	Bu <sub>4</sub> NOH	2	+	
salicylic acid	malonic acid	Bu <sub>4</sub> NOH	2	+	
salicylic acid	succinic acid	Bu <sub>4</sub> NOH	2	+	
salicylic acid	tartaric acid	Bu <sub>4</sub> NOH	2	+	
salicylic acid	phthalic acid	Me <sub>4</sub> NOH	2	+	precipitate
salicylic acid	phthalic acid	Bu <sub>4</sub> NOH	3	+	
salicylic acid	isophthalic acid	Bu <sub>4</sub> NOH	2	+	
salicylic acid	terephthalic acid	Bu <sub>4</sub> NOH	2	+	
p-isopropyl- benzoic acid	terephthalic acid	Me <sub>4</sub> NOH	2	+	precipitate (pyr.-benzene (2:1 v/v))

<sup>a</sup> Bu<sub>4</sub>NOH = tetrabutylammonium hydroxide

titrations, *viz.* 1:10 (equiv./equiv.). Optimum results can only be expected when both compounds are present in approximately equal amounts.

#### d. Two dibasic acids in non-solvating media

In general the principal condition which must be fulfilled in order to resolve a mixture of two dibasic acids is that one of the compounds should give an N-shaped titration curve and the other a chair-shaped one. It is not important whether this difference in shape is obtained with or without the aid of precipitate formation (Figs. 5 and 6), the extent of the difference determining the success of the titration.

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TABLE IV

TITRATION OF TWO DIBASIC ACIDS IN NON-SOLVATING MEDIA

Compound A	Compound B	Base	Solvent	Number of equivalence points	Resolution possible(+) or impossible(-)	Remarks
oxalic acid	succinic acid	Me <sub>4</sub> NOH	DMF	3	+	precipitate
oxalic acid	succinic acid	Bu <sub>4</sub> NOH	pyridine	2	—	
oxalic acid	adipic acid	Me <sub>4</sub> NOH	DMF	2	—	precipitate
oxalic acid	adipic acid	Bu <sub>4</sub> NOH	pyridine	1	—	
oxalic acid	fumaric acid	Me <sub>4</sub> NOH	DMF	2	—	precipitate
oxalic acid	fumaric acid	Bu <sub>4</sub> NOH	pyridine	3	+	
oxalic acid	maleic acid	Me <sub>4</sub> NOH	DMF	3	+	precipitate
oxalic acid	maleic acid	Bu <sub>4</sub> NOH	pyridine	2	—	
oxalic acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
succinic acid	maleic acid	Me <sub>4</sub> NOH	DMF	3	+	
succinic acid	maleic acid	Bu <sub>4</sub> NOH	pyridine	2	—	
adipic acid	maleic acid	Me <sub>4</sub> NOH	DMF	2	—	
adipic acid	maleic acid	Bu <sub>4</sub> NOH	pyridine	4	+	
adipic acid	phthalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
fumaric acid	maleic acid	Me <sub>4</sub> NOH	DMF	3	+	
fumaric acid	maleic acid	Me <sub>4</sub> NOH	pyridine	3	+	precipitate
fumaric acid	maleic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
fumaric acid	isophthalic acid	Me <sub>4</sub> NOH	DMF	1 (2)	— (+)	
fumaric acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine	2	—	
maleic acid	isophthalic acid	Me <sub>4</sub> NOH	DMF	3	+	
maleic acid	isophthalic acid	Me <sub>4</sub> NOH	pyridine	3	+	precipitate
maleic acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
phthalic acid	adipic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
phthalic acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
phthalic acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine-benzene	3	+	precipitate
phthalic acid	isophthalic acid	Bu <sub>4</sub> NOH	pyridine-DMF-benzene	3	+	
phthalic acid	isophthalic acid	Me <sub>4</sub> NOH	pyridine-benzene	3	+	
phthalic acid	isophthalic acid	Me <sub>4</sub> NOH	pyridine-DMF-benzene	3	+	precipitate
phthalic acid	terephthalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
phthalic acid	terephthalic acid	Bu <sub>4</sub> NOH	pyridine-benzene	3	+	precipitate
phthalic acid	terephthalic acid	Me <sub>4</sub> NOH	pyridine-benzene	1	—	precipitate
phthalic acid	terephthalic acid	Bu <sub>4</sub> NOH	pyridine-DMF-benzene	3	+	
phthalic acid	terephthalic acid	Me <sub>4</sub> NOH	pyridine-DMF-benzene	3	+	precipitate
isophthalic acid	oxalic acid	Bu <sub>4</sub> NOH	pyridine	3	+	
isophthalic acid	maleic acid	Me <sub>4</sub> NOH	DMF	3	+	
isophthalic acid	terephthalic acid	Bu <sub>4</sub> NOH	pyridine-DMF-benzene	2	—	
isophthalic acid	terephthalic acid	Me <sub>4</sub> NOH	pyridine-DMF-benzene	3	+	precipitate

Resolution requires that at least 3 equivalence points can be determined (Table IV), of which the first corresponds to the half-neutralization of both compounds and the second and third to the titration of the second functions of the respective acids. Fig. 5 gives an example of such a titration curve. At the first equivalence point the first acid groups of both oxalic and succinic acid are neutralized. Then the second acid group of oxalic acid is titrated with the formation of a sparingly soluble neutral salt. Finally, the third end-point corresponds to the neutralization of the remaining acid group of the succinic acid.

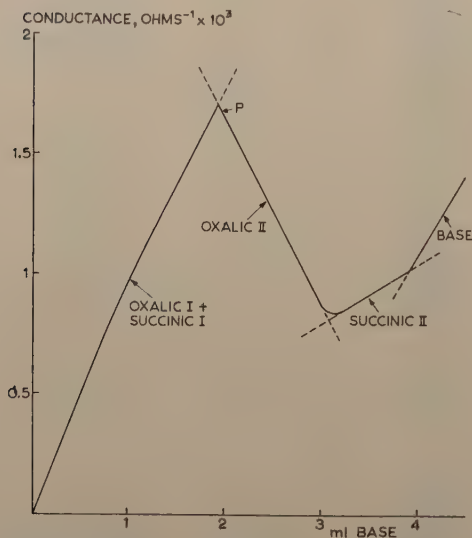


Fig. 5. Titration of a mixture of oxalic acid and succinic acid in DMF with tetramethylammonium hydroxide.  
(*p* = precipitate formation)

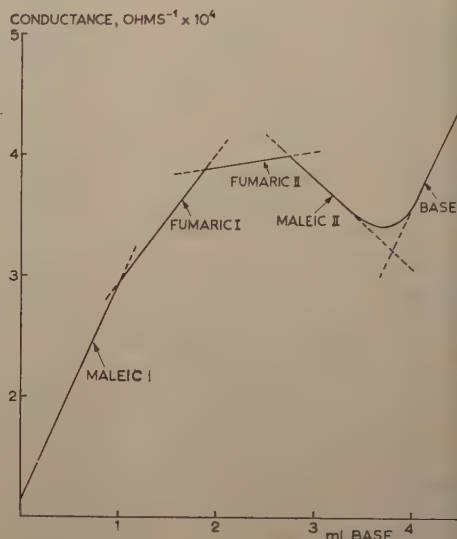


Fig. 6. Titration of a mixture of fumaric and maleic acid in pyridine with tetrabutylammonium hydroxide.

It must be pointed out, however, that the sequence in which the second acid groups are titrated is generally the reverse of that given in the foregoing example. As a rule the proton with the highest acid strength (in this case that of succinic acid) is first titrated, followed by the weaker one, just as in aqueous solutions. This is illustrated in Fig. 6. Four end-points are observed, although the first one is rather indistinct. The first equivalence point corresponds to the neutralization of the strongest acid in the mixture, *i.e.* the first proton of maleic acid. The second and third equivalence points relate to the fumaric acid and the last end-point to the weakest acid, *viz.* the second proton of the maleic acid.

The reverse sequence in the case of the first example (Fig. 5) is caused by the insolubility of the neutral tetramethylammonium oxalate in the solvent used.

Another example in which precipitate formation changes the order of titration involves the resolution of a mixture of isophthalic and terephthalic acid in a mixed solvent (Fig. 7). Three distinct end-points are obtained, the first and second corresponding to the half-neutralization and the total titration of the terephthalic acid, respectively, while the third corresponds to the total acidity of the mixture. A less

distinct break between the second and the third end-point does not correspond to the half-neutralization of the isophthalic acid and attempts to improve this titration were not successful. Moreover, the inflection observed between the first and second end-points cannot be used analytically.

When tetrabutylammonium hydroxide is used for this titration no precipitate is formed. Hence, only two end-points are obtained and resolution of these acids of approximately equal strength is impossible; the first end-point corresponds to half-neutralization of both the isophthalic and the terephthalic acid, the second to the total acidity.

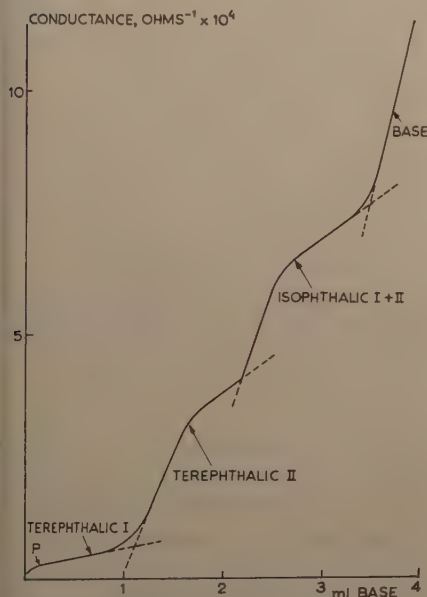


Fig. 7. Titration of a mixture of isophthalic acid and terephthalic acid in a pyridine-DMF-benzene mixture (16:4:5 v/v) with tetramethylammonium hydroxide. (*p* = precipitate formation)

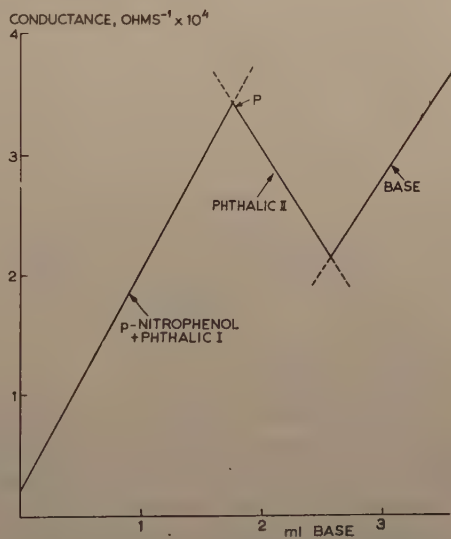


Fig. 8. Titration of a mixture of *p*-nitrophenol and phthalic acid in DMF with potassium methoxide. (*p* = precipitate formation)

## 2. Binary mixtures of carboxylic and phenolic acids

In general phenolic acids can only be titrated with potassium (sodium or lithium) methoxide, using pyridine as a solvent (*cf.* Table I in ref. 1). Hence, in the resolution of acid mixtures containing these compounds only metal bases can be used. The few carboxylic acids that can be determined with these bases in pyridine all give rise to precipitate formation. In consequence, the equivalence points in the titration curves are not usually sufficiently marked for analytical purposes.

Generally speaking, mixtures of carboxylic and phenolic acids can only be determined with sufficient accuracy by means of potentiometric titration in fairly basic solvents<sup>6,7</sup> or by high-frequency titration in alcoholic media<sup>8</sup>. Phenolic compounds which are more acidic than the alkyl phenols are an exception. Phenols with a negative substituent in the *ortho*- or *para*-position belong to this category. The determina-

tion of *p*-nitrophenol has been mentioned as an example. Not only pyridine but also DMF can be used as a solvent in the titration of this compound. Hence, it is possible to resolve mixtures of *p*-nitrophenol and dibasic acids which give insoluble neutral alkali salts in DMF (Fig. 8).

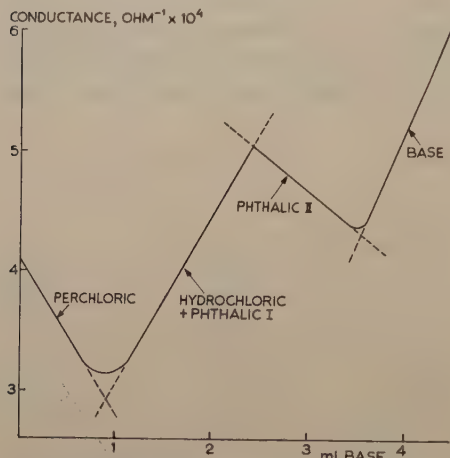


Fig. 9. Titration of a mixture of perchloric acid, hydrochloric acid and phthalic acid in pyridine with tetrabutylammonium hydroxide.

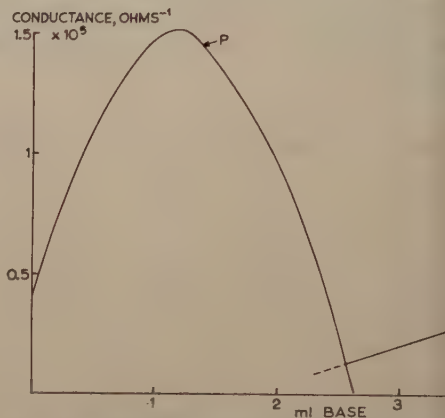


Fig. 10. Titration of diphenylolpropane in pyridine with potassium methoxide. (*p* = precipitate formation)

### 3. Ternary mixtures of acids

In the preceding section we have only mentioned the resolution of mixtures of acids that are weak from the conductometric point of view, *i.e.* acids which are slightly ionized in the media considered. During the titration of these acids the conductance of the solution always increases up to the (first) equivalence point because of the formation of a more strongly ionized salt. However, when strong acids are considered, *i.e.* acids which are mainly ionized, the conductance is at first fairly high; during the titration it decreases by salt formation until the equivalence point is reached and then increases normally owing to the excess of strong base. Examples of acids that are strongly ionized even in weakly basic solvents are perchloric and picric acid; sulphonic acids are of moderate strength in pyridine.

From the foregoing it is obvious that ternary acid mixtures consisting of a strong monobasic, a weak monobasic and a (weak) dibasic acid can be resolved conductometrically under suitable conditions. The result of such an analysis is shown in Fig. 9; the strongly acidic compound, perchloric acid, is neutralized during the period represented by the descending part of the curve, then the weak hydrochloric acid and one group of the phthalic acid titrated, and finally the second group of the dibasic constituent. (This procedure might be useful for the determination of the perchloric acid content of commercial-grade solutions (see under 4)).

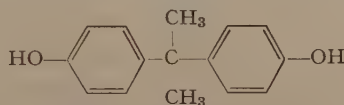
### 4. Some practical applications of non-aqueous conductometric titrations

The conductometric titrations in non-aqueous solutions have been applied to the determination of 2 organic acids and 2 inorganic compounds. Although, strictly

speaking, the latter do not belong to the class of acids studied, they have nevertheless been included because their behaviour under the particular circumstances is analogous to that of the organic acids.

a. *Diphenylolpropane*. In the first paper of this series<sup>1</sup> it was shown that the titration of phenolic compounds in pyridine with potassium methoxide gives satisfactory results. Both alkyl phenols and salicylic acid could be determined with a relative accuracy of 2% or better.

Recently it has been found that bivalent phenols like resorcinol can also be titrated in this way. The bipotassium salts of these compounds are insoluble in pyridine (*cf.* salicylic acid) but nevertheless a distinct equivalence point (the second one) is obtained. On this basis an analytical method has been developed for *p-p*-diphenylolpropane (DPP, Bisphenol A), a base material for the preparation of epoxy-resins.



The sample was dissolved in pyridine and titrated with potassium methoxide which was also dissolved in pyridine<sup>1</sup>. Fig. 10 shows the titration curve obtained. The solubility of the bipotassium salt of DPP in pyridine is only moderately low and the amount of precipitate thus depends strongly on the initial concentration of the phenolic compound.

The break in the curve is caused by a change from a decreasing conductance by precipitation to an increasing one by addition of excess of methoxide, so that a successful analysis is clearly only possible when total precipitation occurs at the end-point. When the solution is too dilute, the break in the titration curve is obtained after the stoichiometric amount of base has been added, *i.e.* when the solubility product has been exceeded (common-ion effect). But when the DPP concentration is high, methoxide may be occluded in the precipitate, again resulting in a high consumption of base. Consequently the initial DPP concentration must be chosen within certain limits. It has been found that at concentrations between 60 and 200 mg/50 ml of pyridine, the results differ less than 0.5% from the theoretical values.

Salicylic acid was used originally for the standardization of the titrant; the same limitations regarding the concentration were valid as for the DPP. The minimum amount of salicylic acid required to obtain results differing less than 0.5% from theory was 120 mg/50 ml of pyridine.

For practical purposes it is more convenient to standardize against a compound which gives no precipitate and can therefore be used in any concentration.  $\beta$ -Naphthol proved to be a very suitable standard. It can easily be purified by recrystallization from water (melting point 122°, *corr.*) and is fairly stable against oxidation by air. The titration curve of  $\beta$ -naphthol with potassium methoxide is given in Fig. 11 of the first paper of this series<sup>1</sup>.

From what has been said in the preceding sections it is clear that in this determination all phenols and stronger acids interfere.

b. *Naphthenic acids*. The conductometric titration also provides a simple and fairly

accurate determination of naphthenic acids in oil products. The base used is sodium or potassium methoxide in methanol-benzene (1:4 v/v). Suitable solvent mixtures are pyridine-DMF (1:1 v/v) or benzene-DMF (1:1 v/v). In the last medium a precipitate is formed but this does not interfere with the determination.

The shape of the curve is similar to that obtained for the titration of an acid of moderate strength in pyridine (*cf.* Fig. 1 in the first paper of this series<sup>1</sup> relating to formic acid).

c. *Perchloric acid.* The perchloric acid content of commercial solutions which contain approx. 60% of the acid can be determined conductometrically. A normal acid-base titration is not sufficient because of contamination by the decomposition product, hydrochloric acid.

The classical method for the determination of perchloric acid and perchlorates is by reduction with stannous chloride followed by back-titration of the excess with permanganate<sup>9</sup>. Chlorides, unless present in very low concentrations, interfere in this titration.

The conductometric determination, on the other hand, is not disturbed by hydrochloric acid, which is only weakly acidic in a pyridine solution. Moreover, it is possible to estimate the amount of hydrochloric acid present, as outlined above (see under 3). The addition of a suitable known amount of succinic acid, which can be obtained in an analytical reagent grade, allows both the standardization of the base used (tetrabutylammonium hydroxide) and the determination of the perchloric and hydrochloric acid to be done in one single titration.

The small amount of water introduced by dissolving the aqueous perchloric acid sample has little influence on the shape of the titration curve.

d. *Mixtures of inorganic acids containing sulphuric acid.* Mixtures of sulphuric acid and a (strong) monobasic inorganic acid like hydrochloric or nitric acid can be resolved in pyridine in the same way as described under 1,c for organic compounds, because these inorganic acids are only slightly ionized in weakly basic solvents.

The potentiometric titration of mixtures of strong acids containing sulphuric acid has recently been described by CUNDIFF AND MARKUNAS<sup>5</sup>, who recommend pyridine as the most stable solvent. However HIGUCHI AND REHM<sup>10</sup> performed the titration of these acids conductometrically in glacial acetic acid with alkali acetates as bases. From the results given by these authors and from our findings, it would appear that for monobasic acid-sulphuric acid mixtures the conductometric or potentiometric titration in pyridine with tetrabutylammonium hydroxide is to be preferred to the one in acetic acid (the conductometric titration curve of sulphuric acid in pyridine has about the same shape as that of succinic acid<sup>3</sup>).

Small amounts of water do not interfere with these titrations.

#### CONCLUSIONS

Conductometric titrations in non-aqueous media offer many possibilities for simple and accurate differentiating determinations of acids. Single compounds as well as mixtures can be satisfactorily analyzed under suitable conditions; if these are full-filled, conductometry can easily compete with potentiometry.

In general tetrabutylammonium hydroxide is the most versatile base, but in some

special applications only alkali methoxides can be used. The most favourable solvent is pyridine, though in many cases dimethylformamide-benzene mixtures may be used instead.

Mixtures containing inorganic acids can be resolved in the same way as those with organic compounds.

#### ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP and the late Mr. P. J. LAFARGUE who skilfully carried out many of the experiments. They also wish to express their gratitude to Dr. Ir. P. N. DEGENS JR. for his stimulating interest in this investigation.

#### SUMMARY

A detailed study has been made of non-aqueous conductometric titrations suitable for the resolution of acid mixtures. The optimum conditions for the various determinations with respect to base and solvent are extensively discussed. The applications include determinations of diphenylolpropane, naphthenic acids, perchloric acid and mixtures containing sulphuric acid.

#### RÉSUMÉ

Dans le présent article les auteurs passent en revue les méthodes de titrage conductométrique de mélanges d'acides dans des solutions non-aqueuses. Ils discutent d'une façon détaillée les conditions optimales pour les différentes déterminations par rapport à la base et au solvant.

#### ZUSAMMENFASSUNG

Die vorliegende Arbeit gibt eine ausführliche Übersicht über Methoden zur Konduktometrischen Titration von Säuregemischen in nichtwässrigen Lösungen. Die optimalen Bedingungen für die verschiedenen Bestimmungen im Hinblick auf Base und Lösungsmittel werden eingehend besprochen.

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## THE SEPARATION OF HYPONITRITE FROM NITRITE, NITRATE AND HYDROXYLAMINE BY PAPER CHROMATOGRAPHY

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### INTRODUCTION

Recent work in nitrate assimilation of micro-organisms has shown that nitrite, hyponitrite and hydroxylamine are likely intermediates of metabolism<sup>1,2</sup>. This investigation was undertaken as a preliminary to the metabolic studies, and was chiefly concerned with obtaining a separation between nitrite and hyponitrite.

The difficulty of detection of these two substances in the presence of one another is well known, and is caused mainly by the instability of hyponitrite (particularly in acid solutions), and by the fact that colours obtained with certain reagents, such as sulphanilamide-N-(1-naphthyl)ethylenediaminedihydrochloride<sup>3</sup> and resorcinol-periodate<sup>4</sup>, depend upon the formation of nitrite from hyponitrite.

In this work an eluant was developed which resolved mixtures of hyponitrite with nitrite, nitrate or hydroxylamine in alkaline conditions. Under these conditions hyponitrite was stabilized during the period of elution.

### EXPERIMENTAL SECTION

#### *Preparation of sodium hyponitrite*

This was carried out by a modification of the method of ADDISON *et al.*<sup>5</sup>. Sodium amalgam was prepared by adding small pieces of sodium metal to warm mercury in a silica crucible until the hot liquid began to solidify. The temperature of the amalgam was then raised until it was fused and a scum of molten sodium hydroxide, carbonate etc. formed on the surface. Most of this adhered to the walls of the crucible when the amalgam was agitated. The remaining bright molten metal was poured into petroleum ether and broken up into pieces in a mortar. The resulting metal amalgam (which was only slowly acted upon by water) was heated with a little distilled water to 80° under nitrogen for a short time and then washed in quick succession with cold distilled water, ethanol, acetone and petroleum ether. It was stored under petroleum ether until required for use. By this procedure a source of carbonate contamination in the sodium hyponitrite, which in the author's opinion is far more serious than aerial contamination, was eliminated.

Sodium nitrite (20 g) was dissolved in water (60 ml) and added dropwise via a tap-funnel to the purified sodium amalgam in a conical flask. Provision was made for a thermometer to dip into the reacting mixture and the bung was also fitted with entry and exit tubes for nitrogen to displace air from the flask. The temperature of

the reacting mixture was kept at 60°–80° as, according to MELLOR<sup>6</sup>, a maximum yield of hyponitrite is obtained below 100°.

The addition of sodium nitrite was stopped just before the amalgam had completely liquified, and the reaction was allowed to proceed for a further 5–10 min. The mixture was then cooled and the remaining liquid amalgam was separated. The aqueous portion was filtered rapidly by suction through a No. 541 paper and poured into a 20-fold excess of ethanol under nitrogen. After allowing this mixture to stand 1 h, the precipitated sodium hyponitrite was filtered off by suction (No. 541 paper), washed with ethanol and ether and dried in vacuo over  $P_2O_5$  in a desiccator for 24 h. The product appeared to be of a high degree of purity because: (1) silver nitrate produced a bright yellow flocculent precipitate with a fresh solution of the salt, (2) nitrite was not detected when a concentrated solution of the salt was analyzed by paper chromatography (see below), (3) the material was shown to be free from carbonate by boiling it with water for a few minutes to destroy  $N_2O_2^{-2}$  followed by the addition of a few drops of fresh baryta solution. No turbidity was observed.

The compound, when dry, could be kept indefinitely in a stoppered container.

#### *Paper chromatography of hyponitrite-containing mixtures*

Freshly prepared solutions of sodium hyponitrite in 2 *N* NaOH were mixed with sodium nitrite, nitrate, or a solution of hydroxylamine sulphate in sodium hydroxide. Resolution of the mixtures was effected by downward chromatography on acid washed Whatman No. 1 paper strips in an eluant containing: ethanol 70 ml, water 30 ml, sodium hydroxide 2 g. During elution the eluant was frontally analyzed on the chromatogram. Hyponitrite was contained within the upper sodium hydroxide zone, while nitrite, nitrate and hydroxylamine moved with the ethanol–water zone further down the chromatogram. Approximate  $R_F$  values were: 0.1 for  $N_2O_2^{-2}$  and 0.5–0.6 for  $NO_2^-$ ,  $NO_3^-$  and  $NH_2OH$ . Hyponitrite and nitrite were developed by using a modification of VEPŘEK-SÍŠKA's reagent<sup>4</sup>. Equal volumes of solutions of resorcinol in glacial acetic acid and sodium meta-periodate in water were mixed as required and sprayed on to the dried chromatogram. Brown spots were obtained which gave an orange fluorescence in U.V. light, and which darkened on standing, or by exposing them to ammonia. 1  $\mu g$  of  $N_2O_2^{-2}$  was easily detected on the chromatogram by fluorescence in U.V. light after the resorcinol-periodate treatment, and 1  $\mu g$  of  $NO_2^-$  was seen in daylight after the same treatment.

When sodium hydroxide was replaced by ammonia in the eluant, double spotting was observed with nitrite, due, presumably, to competition between sodium and ammonia for the anion.

Nitrate was not detected by the resorcinol-periodate reagent but appeared as a fluorescent spot in U.V. light after dipping the chromatogram in an ethereal solution of 8-hydroxyquinoline (oxine) or spraying the paper with a solution of nitron in 60% acetone followed by exposure of the dried chromatogram to ammonia. The nitron test was a modification of the method used by POLLARD<sup>7</sup> for detecting nitrate. Nitrite did not fluoresce with nitron but did so with oxine in U.V. light. Nitrite and nitrate presumably move as the sodium salts as sodium was present in the excised spots, whereas other portions of the chromatogram (with the exception of the frontally-analyzed NaOH band) were free from this metal.

Hydroxylamine was detected by spraying the damp chromatograms with either

the resorcinol-periodate reagent (orange-brown band) or alkaline copper citrate solution (brownish yellow band on a blue background). The latter reagent was prepared as required by mixing solutions of cupric chloride and citric acid and adding sodium hydroxide until a precipitate began to form in the dark blue liquid. If the chromatogram was dried completely, no hydroxylamine could be detected owing, presumably, to its volatilization from the paper.

The chromatographic method was found to be useful for testing the purity of hyponitrite material prepared from other sources. Samples of silver hyponitrite, which had been made by the interaction of hydroxylamine sulphate and sodium nitrite and precipitated with silver nitrate, were analysed by decomposing them with a few drops of a saturated solution of sodium chloride and stabilizing the liberated  $\text{N}_2\text{O}_2^{-2}$  with 1-2 drops of 12 *N* NaOH. After filtering, spots of the solution were analysed on paper strips, and the results showed that even when the silver compound had been thoroughly washed with water until the washings ceased to give a definite  $\text{NO}_2^-$  reaction with the sulphanilamide-naphthyl reagent<sup>3</sup>, traces of  $\text{NO}_2^-$  could be detected on the paper strip. This, presumably, was due to the adsorption of  $\text{NO}_2^-$  ions by silver hyponitrite during the precipitation.

All samples of sodium hyponitrite gave, on chromatograms developed with the resorcinol-periodate reagent, a weak brown spot of unknown origin at  $R_F$  0.8-0.9. The phenomenon also occurred when spots of the strongly alkaline solution obtained after amalgam reduction of the nitrite were run on paper strips, but the spot was weaker than that obtained from samples of precipitated sodium hyponitrite. The substance responsible for this phenomenon must therefore be co-precipitated with sodium hyponitrite when the amalgam reduced solution is poured into an excess of ethanol. Impurities in the starting materials were ruled out because the spot was not obtained when concentrated solutions of  $\text{NaNO}_2$  or sodium amalgam in water were run separately on paper strips.

The  $R_F$  value of this spot, and its stability in this region precludes it from being due to  $\text{N}_2\text{O}_2^{-2}$  or  $\text{NH}_2\text{OH}$ ; failure to give a colour with the sulphanilamide-naphthyl reagent unless  $\text{NaIO}_4$  solution was added suggests that it is not due to  $\text{NO}_2^-$ , but is oxidized to the latter by the periodate. Hydrazine and (sodium) azide were also ruled out because their behaviour on paper chromatograms was not compatible with that of the uncharacterized substance ( $R_F$  values:  $\text{NaN}_3$  0.62,  $\text{N}_2\text{H}_4$  streaks to 0.5).

Sodium hyponitrite (200 mg) was dissolved in a minimum of 2 *N*  $\text{NaOH}$ , and the solution placed on a column of dry cellulose. Elution was carried out with the ethanol-water-sodium hydroxide eluant and the first few milliliters of eluant at breakthrough were found by chromatographic analysis to contain a concentration of the uncharacterized material. When this eluant was evaporated over  $\text{P}_2\text{O}_5$  in vacuo, analysis by paper strip chromatography showed that only  $\text{NO}_2^-$  was present in the residue.

These observations suggest that the material is a reduction product of  $\text{NO}_2^-$  which is converted back to the latter by aerial oxidation.

#### SUMMARY

The preparation of carbonate-free sodium hyponitrite and the resolution by paper chromatography of mixtures of sodium hyponitrite with sodium nitrite, nitrate, or hydroxylamine are  
*References p. 459*

described. Observations were made upon an uncharacterized impurity which was present in very small amounts in the prepared sodium hyponitrite samples.

### RÉSUMÉ

L'auteur décrit la préparation d'un hyponitrite de sodium, exempt de carbonate et la séparation de cet hyponitrite d'avec nitrite, nitrate et hydroxylamine, par chromatographie sur papier.

### ZUSAMMENFASSUNG

Es wird die Darstellung eines carbonat-freien Natriumhyponitrits sowie die papierchromatographische Trennung von Gemischen von Natriumhyponitrit, Natriumnitrit, Natriumnitrat und Hydroxylamin beschrieben.

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## GRAVIMETRIC DETERMINATION OF COBALT AND NICKEL, AND THEIR SEPARATIONS FROM COPPER WITH N-BENZOYLPHENYLHYDROXYLAMINE

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N-benzoylphenylhydroxylamine was suggested by SHOME<sup>1</sup> as a reagent for the analysis of many metals and has been used for the gravimetric determination of copper, iron, aluminium and titanium<sup>2</sup>, and for the colorimetric estimation of vanadium<sup>3</sup>. In the present investigation cobalt and nickel are precipitated separately with this reagent from their hot buffered solutions. The metal complexes correspond to the formulae  $\text{Co}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$  and  $\text{Ni}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N})_2$ , and can be weighed directly. By adjusting the pH of the solutions it is possible to separate either cobalt or nickel from copper and to determine the component metals of any of the mixtures.

### SOLUTIONS USED IN THE DETERMINATION OF THE METALS

#### *Metals to be determined*

Separate standard solutions of cobalt sulphate, nickel ammonium sulphate and copper sulphate were prepared to contain 1.05 mg of cobalt, 1.22 mg of nickel and 1.32 mg of copper respectively per ml.

All the chemicals used were of A.R. quality.

*References p. 462*

## DETERMINATION OF COBALT AND NICKEL

A known quantity of the cobalt or nickel solution (20 to 30 ml) was diluted to 300 ml with distilled water and heated to boiling. (In the case of cobalt, 10 ml of a 2 % hydroxylamine hydrochloride solution were added to prevent subsequent formation of any cobaltic complex.) Benzoylphenylhydroxylamine (0.25 to 0.3 g) solution in alcohol (10 to 15 ml) was slowly added to the hot solution of the metal. A 10 % sodium acetate solution (5 to 10 ml) was added to maintain the pH of the solution between 5.5 and 6.5, estimated with pH paper. The mixture was stirred occasionally during one hour on a boiling water-bath. The precipitate was then filtered, washed, and ignited to the oxide. The cobalt oxide was heated with a mixture of concentrated nitric and sulphuric acids and weighed as cobalt sulphate; the nickel was weighed as nickelous oxide.

The results (Table I) indicate that cobalt and nickel ions are quantitatively precipitated with benzoylphenylhydroxylamine and can be weighed as cobalt sulphate and nickel oxide respectively.

TABLE I

DETERMINATION OF NICKEL OR COBALT BY WEIGHING AS NICKEL OXIDE OR COBALT SULPHATE

<i>Metal taken (g)</i>	<i>Weight of ppt. (g)</i>	<i>Metal found (g)</i>	<i>Error (g)</i>
Co		Co	
0.02623	0.06860	0.02610	— 0.00013
0.03147	0.08230	0.03130	— 0.00017
0.02518	0.06650	0.02530	+ 0.00012
0.02413	0.06310	0.02400	— 0.00013
Ni		Ni	
0.06086	0.07700	0.06050	— 0.00036
0.05852	0.07460	0.05861	+ 0.00009
0.05628	0.07180	0.05641	+ 0.00013
0.05384	0.06880	0.05406	+ 0.00022
0.04856	0.06160	0.04841	— 0.00015

pH of solution = 5.5 to 6.5.

TABLE II

DETERMINATION OF COBALT AND NICKEL BY WEIGHING THE METAL COMPLEXES DIRECTLY

<i>Metal taken (g)</i>	<i>Weight of ppt. (g)</i>	<i>Metal found (g)</i>	<i>Error (g)</i>
Co			
0.03147	0.25710	0.03139	— 0.00008
0.02938	0.24110	0.02943	+ 0.00005
0.02833	0.23290	0.02834	+ 0.00001
0.02729	0.22220	0.02713	— 0.00016
0.02623	0.21600	0.02637	+ 0.00014
Ni			
0.03048	0.24920	0.03030	— 0.00018
0.02926	0.24180	0.02941	+ 0.00015
0.02804	0.23160	0.02816	+ 0.00012
0.02682	0.21980	0.02672	— 0.00010
0.02438	0.20150	0.02450	+ 0.00012

In another series of experiments, cobalt and nickel were precipitated separately with benzoylphenylhydroxylamine as described above. The precipitate was then filtered on a No. 3 sintered glass crucible, washed well with hot water and dried at 110–120° to constant weight. The metal contents were calculated on the basis that the precipitates contained 12.21% of cobalt and 12.16% nickel respectively.

It can be seen from Table II that the precipitates of cobalt and nickel with benzoylphenylhydroxylamine can be determined by weighing the precipitates directly. At pH values above 6.5, the precipitates form hard lumps (and in the case of nickel the solution also becomes coloured) whereas below pH 5.5 the precipitation of the metals is incomplete. If the cobalt is precipitated without prior addition of hydroxylamine hydrochloride the results obtained are slightly high, probably owing to the formation of a small amount of cobaltic complex in the precipitate.

#### GRAVIMETRIC SEPARATIONS OF COBALT AND NICKEL FROM COPPER

A mixture containing known amounts of copper sulphate and either cobalt sulphate or nickel ammonium sulphate was diluted to 400 ml with distilled water. Sulphuric acid (4 to 5 ml of 1.5 *N*) and 10% sodium acetate solution (15 ml) were then added to adjust the pH to about 4.0. The solution was heated to boiling and copper was precipitated by the gradual addition of benzoylphenylhydroxylamine (0.25 to 0.35 g) dissolved in alcohol (5 to 10 ml). The copper precipitate was heated on the water-bath for one hour with occasional stirring, filtered on a No. 3 sintered glass-crucible, washed well (the wash-water contained sufficient sodium acetate and sulphuric acid in distilled water to maintain the pH at about 4.0), and dried at 110–120° to constant weight. The copper content of the precipitate was calculated on the basis that the precipitate contained 13.03% of copper.

The filtrate and washings were evaporated to about 300 ml and filtered. During

TABLE III  
SEPARATION OF COBALT FROM COPPER

Mixture No.	Metal taken (g)		Wt. of ppt. (g)		Metal found (g)		Error (g)	
	Cu	Co	Cu	Co	Cu	Co	Cu	Co
1	0.03311	0.02623	0.25329	0.21550	0.03296	0.02631	−0.00015	+0.00008
2	0.03973	0.03147	0.30600	0.25800	0.03987	0.03150	+0.00014	+0.00003
3	0.02781	0.02833	0.21180	0.23250	0.02760	0.02839	−0.00021	+0.00006
4	0.03046	0.02938	0.23480	0.23400	0.03060	0.02930	+0.00014	−0.00008
5	0.02649	0.02623	0.20500	0.21320	0.02679	0.02603	+0.00030	−0.00020

TABLE IV  
SEPARATION OF NICKEL FROM COPPER

Mixture No.	Metal taken (g)		Wt. of ppt. (g)		Metal found (g)		Error (g)	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
1	0.03973	0.03048	0.30590	0.25160	0.03985	0.03051	+0.00012	+0.00003
2	0.03311	0.02926	0.25480	0.24020	0.03320	0.02914	+0.00009	−0.00012
3	0.03046	0.02682	0.23200	0.22180	0.03036	0.02690	−0.00010	+0.00008
4	0.02781	0.02804	0.21510	0.22960	0.02801	0.02786	+0.00020	−0.00018
5	0.02649	0.02438	0.20250	0.20110	0.02638	0.02440	−0.00011	+0.00002

the concentration of the filtrate an organic precipitate appeared in the solution, probably owing to the prolonged heating of the reagent solution in air. Before the subsequent determination of cobalt, 20 ml of 2% hydroxylamine hydrochloride solution were added. Cobalt or nickel in the solution was then determined as described above.

The results in Tables III and IV indicate that cobalt or nickel can be separated from copper and the two component metals of the mixtures can be determined separately.

#### CONCLUSIONS

Cobalt and nickel can be determined with N-benzoylphenylhydroxylamine, the precipitates being directly weighable. For the determination of cobalt the present method offers the advantage over the  $\alpha$ -nitroso- $\beta$ -naphthol method that the precipitate need not be ignited and converted to cobalt sulphate. By the methods described, cobalt or nickel can be separated from copper and the individual metals determined by direct weighing. The procedure is simple and the organic reagent can be prepared easily and stored indefinitely.

#### ACKNOWLEDGEMENT

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#### SUMMARY

N-Benzoylphenylhydroxylamine can be used for the gravimetric determination of cobalt and nickel. The precipitates can be weighed as such, or ignited and weighed as cobalt sulphate or nickelous oxide. Cobalt or nickel can be separated from copper with the reagent.

#### RÉSUMÉ

La N-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du cobalt et du nickel. Ces deux cations sont précipités séparément et peuvent être séparés d'avec le cuivre.

#### ZUSAMMENFASSUNG

Kobalt und Nickel können mit Hilfe von N-Benzoylphenylhydroxylamin gravimetrisch bestimmt werden. Die beiden Metalle können einzeln gefällt und gleichzeitig von Kupfer abgetrennt werden.

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## DETERMINATION OF ARSENIC IN ORGANIC COMPOUNDS

### RAPID MICRO AND SEMIMICRO METHODS

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The extension of his rapid method for the micro determination of halogens and sulfur in organic compounds<sup>1</sup> to the determination of phosphorus, arsenic and metals was predicted by SCHÖNIGER<sup>2</sup>. In this method, the sample is wrapped in a filter paper envelope, affixed to the end of a platinum wire, and burned in an oxygen-filled flask containing a suitable liquid absorbent for the desired products of combustion. This method has been successfully applied to the determination of phosphorus<sup>3</sup> and mercury<sup>4</sup>. In attempting to extend this method to the determination of arsenic, variable, but consistently low results were obtained. Because the platinum support was pitted, arsenic was presumed to be lost by reaction with the platinum. Replacement of the platinum with a quartz spiral was not satisfactory because the quartz devitrified during the course of a single combustion.

In 1952, ZAK *et al.* prepared 28% chloric acid and used it for the determination of iodinated organic compounds<sup>5</sup> and for the digestion of organic matter in the determination of serum protein-bound iodine<sup>6,7</sup>. Improvements in the technique for serum protein-bound iodine were made by several investigators<sup>8-10</sup>. MCCHESENEY AND HOPPE<sup>11</sup> have adapted this method to the determination of iodine containing radio-paques in tissues. MCCHESENEY AND BANKS<sup>12</sup> used digestion with chloric acid in their determination of sulfur in biological materials.

Because chloric acid oxidizes organic matter smoothly and rapidly at about 180°, it is to be preferred to the more widely used sulfuric acid or sulfuric-nitric acid digestions or alkaline fusions. Excess acid is easily boiled off to leave a perchloric acid solution of the inorganic elements, usually present in one of their higher oxidation states.

#### APPARATUS AND REAGENTS

Most of the apparatus and reagents used are common laboratory items. The following special solutions are needed.

*Chloric acid, 28%.* Prepared by the method of ZAK<sup>7</sup> or of STRICKLAND AND MALONEY<sup>10</sup> if the reagents used in the preparation are of unknown purity.

*Standard 0.005 N trivalent arsenic.* Transfer 247.3 mg of reagent grade arsenic trioxide, previously dried to constant weight at 105°, to a 1000-ml volumetric flask.

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Dissolve the solid in 4 ml of 1 *N* sodium hydroxide, neutralize the solution to phenolphthalein indicator by dropwise addition of 6 *N* hydrochloric acid, then add 50 g of sodium bicarbonate. Dilute to 1000 ml with distilled water, mix well.

*Standardized 0.005 N iodine.* Dissolve 2 g of sodium iodide in 5 ml of distilled water, add 0.65 g of iodine, and agitate until the iodine is dissolved. Dilute to 1000 ml with distilled water, mix well. Standardize by titration against the standard trivalent arsenic solution, using starch indicator.

*Colorimetric reagent.* Mix equal volumes of 2.5% (w/v) ammonium molybdate in water and 1% (w/v) bismuth subcarbonate U.S.P. in 7 *N* sulfuric acid. Immediately before use add 10 g of ascorbic acid per 100 ml of solution. Use of this reagent as directed below will give the optimum acidity for color development. This method is a modification of the procedure suggested by JEAN<sup>13</sup>.

*Standard arsenic solution.* Digest arsenic trioxide or an organic arsenical of known purity with chloric acid as set forth below. Dilute the neutralized digest to produce a solution containing about 10  $\mu$ g of arsenic per ml.

#### DIGESTION WITH CHLORIC ACID

The following digestion is used for both the micro and semimicro determination. Transfer a weighed sample containing 4 to 5 mg of arsenic to a 250-ml glass-stoppered conical flask for the semimicro method, or, transfer a weighed sample containing 0.25 to 0.6 mg of arsenic to a 250-ml conical flask for the micro method. Add 10 ml of chloric acid and digest on a hot plate until heavy white fumes of perchloric acid are produced and the solution is colorless. Do not allow the digest to evaporate to dryness. Remove the flask from the hot plate, cool, add 2 ml of distilled water, 1 drop of phenolphthalein indicator, and neutralize with 10% sodium hydroxide solution (about 5 ml required). Discharge the phenolphthalein color by dropwise addition of 6 *N* hydrochloric acid.

For the digestion of larger amounts of organic matter, 35 ml of chloric acid per gram of sample has been found adequate, but in no case should less than 10 ml of chloric acid be used.

#### SEMIMICRO METHOD

##### *Procedure*

To the neutralized digest add 25 ml of 1 *N* hydrochloric acid, then 1 g of sodium iodide. Stopper the flask, swirl to dissolve the iodide, loosen the stopper, heat on a steambath for 15 min, then cool to room temperature. Discharge the iodine color by titration with approximately 0.005 *N* sodium thiosulfate solution, adding 2 ml of starch indicator toward the end of the titration. Add sodium bicarbonate in small portions to neutralize the acid, then saturate the solution with bicarbonate as shown by the presence of undissolved bicarbonate. Titrate with recently standardized 0.005 *N* iodine solution. Arsenic which has been reduced to the trivalent state by hydriodic acid is quantitatively re-oxidized by iodine to the pentavalent state. The conditions were recommended by FLEURY<sup>14</sup> in his critical review.

##### *Accuracy and reproducibility*

Ten samples of *p*-arsanilic acid (theoretical arsenic content 34.5%), ranging from 6.8 to 13.2 mg in weight, were assayed with the following results in per cent arsenic:

*References p. 467*

34.5, 34.5, 34.3, 34.8, 34.8, 34.7, 34.8, 34.3, 34.6, 34.5; average: 34.6. By the method given by DEAN AND DIXON<sup>15</sup> the 99% confidence interval is  $\pm 0.2$  which gives a 99% confidence level for this method of 6 parts per thousand.

Assays of four samples of *o*-arsanilic acid (theoretical arsenic content 34.5%) ranging from 9.3 to 11.0 mg in weight gave the following results in per cent arsenic: 33.7, 33.5, 33.6, 33.9; average: 33.7. The 99% confidence interval is  $\pm 0.5$  or 15 parts per thousand.

Analyses of other arsenicals are shown in Table I. These samples had been prepared as research compounds at the Sterling-Winthrop Research Institute and may be

TABLE I  
ASSAYS BY SEMIMICRO METHOD

Substance	Sample weight mg	% As found	% As theory	% error
3-2 (hydroxethylureido)-4-hydroxy phenylarsonic acid	21.106	23.46	23.40	+0.3
6,7-dimethoxy-3-nitro-9-(3-diethyl amino-2-hydroxypropylamine-acridine di-(4-glycoly-aminophenylarsonate) (Rutenol <sup>®</sup> )	30.182	15.61	15.31	+2.0
Sodium p-N-glycolylarsanilate tetrahydrate (Quarcy <sup>®</sup> )	11.221	20.74	20.30	+2.2
4-(2-hydroxyethylureido)-phenylarsonic acid	22.783	24.65	24.63	+0.1
0.1 N sodium arsenite solution	1.00 ml	0.373	0.375	-0.5

considered to be at least 97% pure based on elemental analyses for carbon, hydrogen, and nitrogen.

*Application to commercial preparation*

A 750-mg sample of a 7-g suppository which was claimed to contain 250 mg of acetarsone in a glycerinated gelatin base was assayed by the above procedure. Recovery was 103% of claim.

*Interference*

Five ml of conc. hydrochloric acid were added to a sample of *p*-arsanilic acid before digestion to give a calculated initial chloride concentration of about 4 M. Recovery of arsenic was 99.6%.

Because the presence of bismuth in glycobinarsol, U.S.P. (Milibis<sup>®</sup>) gives a yellow bismuth iodide complex which interferes in the titration with thiosulfate, the procedure was modified by the following addition. After reduction of the arsenic with hydriodic acid, 10 ml of a 0.1 M solution of disodium (ethylene dinitrilo) tetra-acetate were added, and the solution cautiously adjusted to about pH 2 with sodium carbonate in order to discharge the color of the bismuth iodide complex. It had been previously determined that this procedure did not affect the titration of trivalent arsenic with iodine. Despite this change, the method gave results for arsenic of only 20 to 35% of the expected value. It was thought that bismuth might interfere in the reduction

of pentavalent arsenic by lowering the effective concentration of iodide, but replacement of the hydrochloric acid and sodium iodide with 1 *N* hydriodic acid was without effect. It is postulated that a bismuth-arsenic-iodide complex is formed which is not as readily reduced by hydriodic acid to arsenic (III) as arsenic(V) iodide.

## MICRO METHOD

*Procedure*

Dilute the neutralized digest to 100 ml in a volumetric flask. In test tubes graduated at 10 ml introduce 2-ml aliquots of the standard arsenic solution, the sample dilution, and distilled water. Dilute each to 7 ml. To each add 2 ml of the colorimetric reagent, dilute to 10 ml, mix the contents of each tube, and allow to stand for 5 min. Read the absorbance in a suitable colorimeter using a filter having a maximum transmittance at 660  $m\mu$ , setting the instrument to zero absorbance with the distilled water blank. The color is stable for at least 1 h. The color produced follows the Beer-Lambert law at least up to 40  $\mu g$  of arsenic in the final 10-ml volume.

TABLE II  
ASSAYS BY MICRO METHOD

Substance	Sample weight mg	Absorbance	% As found	% error
Glycobiarsol, U.S.P.-14.78% As, (Milibis <sup>R</sup> )	5.605	0.253	14.7	—0.6
o-Arsanilic acid-33.7% As	4.860	0.495	33.3	—1.2
	4.205	0.423	32.8	—2.7
	2.224	0.235	34.5	+2.4
4-(2-Hydroxyethylureido)- phenylarsonic acid-24.6% As	2.897	0.221	25.9	+5.3
	2.395	0.186	25.4	+3.3
	2.346	0.180	25.0	+1.6
	2.446	0.186	24.8	+0.8
	2.421	0.186	25.1	+2.0

*Reproducibility and accuracy*

Seven samples of *p*-arsanilic acid, ranging from 1.6 to 4.0 mg in weight, were run, as described above, on different days. The absorbance per mg of arsenic in 10 ml of final dilution measured in a particular set of cells in our colorimeter were: 15.8, 15.1, 15.4, 15.0, 15.4, 15.3, 15.2; average: 15.3. The 99% confidence interval is  $\pm 0.4$  or 26 parts per thousand.

Using the average absorbance per mg of arsenic found for *p*-arsanilic acid, samples of 4-(2-hydroxyethylureido)-phenylarsonic acid found to contain the theoretical 24.6% of arsenic by the semimicro method were assayed by the micro method. Results are shown in Table II. Other compounds not containing their theoretical amount of arsenic are also shown in Table II. It is interesting to note that the sample of Milibis<sup>R</sup>, which could not be assayed by the semimicro method, gave excellent results by the micro method.

### Interference

Phosphorus interferes by formation of a heteropoly blue similar to that formed by pentavalent arsenic. Phosphorus and arsenic, if present together, may be separated and determined, after digestion of the sample with chloric acid, by the method given by JEAN<sup>13</sup>.

### SUMMARY

Rapid micro and semimicro methods for determination of arsenic in organic compounds have been developed using 28% chloric acid as the digesting agent for the organic arsenical. This wet acid digestion procedure does not lead to loss of arsenic even in the presence of 4 M chloride.

The semimicro method completes the assay by reduction of the pentavalent arsenic with iodide, destruction of the iodine liberated with thiosulfate and re-oxidation to pentavalent arsenic with iodine in a buffered solution. The micro method completes the assay by development of a heteropoly molybdenum blue using a single solution reagent at room temperature. The color is reproducible so that only a single calibration curve for the instrument used is necessary.

### RÉSUMÉ

Les auteurs proposent une méthode semimicrochimique et une méthode microchimique pour le dosage de l'arsenic dans des matières organiques. La substance à analyser est attaquée par l'acide chlorique. Le dosage semimicrochimique consiste à réduire l'arsenic (V) par un iodure et à titrer ensuite l'arsenic(III) formé par l'iode. Dans le procédé microchimique, on procède par colorimétrie du bleu de molybdène.

### ZUSAMMENFASSUNG

Es wird eine mikro- und halbmikrochemische Methode zur Bestimmung von Arsen in organischen Substanzen beschrieben. Der Aufschluss der Substanz erfolgt mit Chlorsäure. Bei der Halbmikromethode wird das gebildete Arsen(V) zu Arsen(III) reduziert und dieses mit Jodlösung titriert. Bei der Mikromethode erfolgt die Bestimmung kolorimetrisch nach Bildung von Molybdänblau.

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## COULOMETRIC-ACIDIMETRIC TITRATIONS IN ANHYDROUS ACETIC ACID\*

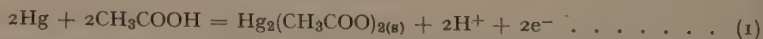
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As pointed out by LINGANE<sup>1</sup>, the extension of coulometric methods to non-aqueous solvents would greatly broaden the practical scope of the technique. However, only a handful of coulometric experiments involving non-aqueous media have been reported. MEYER AND BOYD<sup>2</sup> have described a method for a coulometric Karl Fischer titration in a methanol solution. STREULI<sup>3</sup> and HANSELMAN AND STREULI<sup>4</sup> described a coulometric titration of several amines in acetonitrile. In the latter case the supporting electrolyte was 0.05 *F* lithium perchlorate trihydrate, and the three waters of hydration provided enough water so that its oxidation to oxygen served as the hydrogen ion-producing electrode reaction. HANSELMAN AND STREULI<sup>4</sup> have also used the oxidation of hydroquinone to quinone in acetonitrile to generate hydrogen ion.

The large number of volumetric-acidimetric titrations<sup>5</sup> which have been described in which acetic acid is used as the solvent led us to try to develop a coulometric titration procedure for this solvent in order to make the titration as catholic as possible. The procedure which has resulted combines the advantages of both coulometric and non-aqueous acidimetric titrations. It should be applicable to the determination of  $\mu\text{g}$ -quantities of bases<sup>1</sup> which are too weak to be titratable with acid in aqueous solutions.

The generation of hydrogen ion in anhydrous acetic acid-acetic anhydride mixtures was accomplished by anodically oxidizing a mercury electrode. The predominant electrode reaction which occurs is reaction (1):



The generation of hydrogen ions proceeds with 100% current efficiency in a supporting electrolyte of sodium perchlorate. The mercury(I) acetate which is formed is a stable, insoluble precipitate which accumulates during the titration.

### EXPERIMENTAL

Except for the sodium perchlorate all chemicals used were commercial products of highest purity and were used without further purification.

All batches of sodium perchlorate which were tested by us contained significant amounts of basic impurities which had very deleterious effects on the sharpness of

\* Contribution No. 2470 from the Gates and Crellin Laboratories of Chemistry.

the potentiometric end-point. After one recrystallization from hot acetic acid the impurities were reduced to an acceptably low level and the end-point sharpness was substantially improved.

Hydrogen ions were generated in a supporting electrolyte prepared by dissolving 0.1 formula weight of sodium perchlorate in a solvent consisting of one part (by volume) acetic acid to six parts acetic anhydride.

Standard solutions of base were prepared by dissolving weighed quantities of sodium carbonate or potassium hydrogen phthalate in measured volumes of acetic acid.

The titration cell consisted of a 150-ml beaker fitted with a rubber stopper. The solution in the cell was stirred magnetically. Although the solvent gradually attacked the rubber stopper, no impurities appeared to be introduced into the solution during the time required for a titration (up to 45 min). The mercury-generating anode employed was either a 5-cm<sup>2</sup> amalgamated gold electrode or a mercury pool electrode of approximately 20 cm<sup>2</sup>. Both electrodes functioned well, but the large pool electrode was more suitable for titrations of larger amounts of base because the resulting mercury(I) acetate did not tend to insulate this electrode from the solution. The auxiliary cathode consisted of a platinum wire separated from the body of the solution by a sintered glass tube. The cathode compartment was filled with the same supporting electrolyte as the anode compartment. Hydrogen gas was evolved at the cathode.

The titration was followed potentiometrically by means of a glass electrode and a specially constructed mercury-mercurous acetate reference electrode. The glass electrode was stored in acetic acid when not in use in order to maintain its sensitivity; storage in water or acetic anhydride caused the reproducibility and sensitivity of the electrode to decrease markedly.

An ordinary calomel reference electrode could not be employed not only because chloride ion is titrated as a base in the solvent used, but also because the sodium perchlorate supporting electrolyte causes potassium perchlorate to precipitate at the junction of the calomel reference electrode and spurious potential readings result. The mercury-mercurous acetate reference electrode was prepared by adding excesses of solid mercurous acetate and mercury metal to anhydrous acetic acid, which was saturated with sodium perchlorate. Connection with the solution was accomplished by means of a sodium perchlorate salt bridge.

The potential of the glass-reference electrode pair was measured with the mV-scale of a Leeds and Northrup pH Indicator. The potentials measured had no absolute significance but could be used empirically to detect the end-point of the titration.

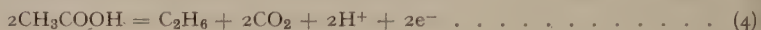
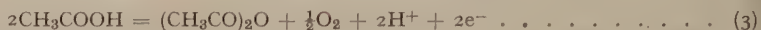
The constant current source was modeled after that described by LINGANE<sup>6</sup>. Even though the resistance of the supporting electrolyte was from 2000 to 6000 Ohms, currents from 1–25 mA were maintained constant to  $\pm 0.05\%$ .

#### THE TITRATION

##### *Hydrogen ion generation current efficiency*

The oxidation of a mercury electrode in anhydrous acetic acid is a very satisfactory means of generating hydrogen ion with 100% current efficiency. This is true because the predominant electrode reaction, (1), as well as the most likely side reactions, (2),

(3), and (4), all correspond to 100% current efficiency for generation of hydrogen ion:



In fact it is not possible to write a reasonable anodic reaction for a mercury electrode in a sodium perchlorate–anhydrous acetic acid electrolyte which does not correspond to 100% current efficiency for hydrogen ion generation. In accordance with this, we observed no difficulty in generating hydrogen ion with 100% current efficiencies with current densities from 0.2–2.0 mA per cm<sup>2</sup>.

### *The detection of the end-point*

After soaking in acetic acid for several h, the glass electrode responded readily to changes in hydrogen ion concentration in the acetic acid–acetic anhydride solvent. A typical titration curve for the titration of *ca.* 0.03 mmoles of potassium hydrogen phthalate in a volume of 75 ml is shown in Figure 1. The potentials adopted by the glass electrode at the start of a titration were reproducible to 2–3 mV for each concentration of base used, and the end-point potentials were equally reproducible. The end-point was taken as the point of maximum slope in a plot of generation time *versus* the potential of the glass electrode.

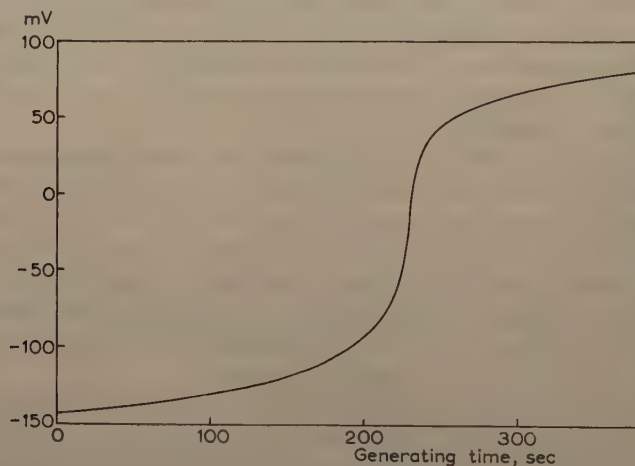


Fig. 1. Potentiometric titration curve for 0.03 mmoles of potassium hydrogen phthalate in 75 ml of acetic acid–acetic anhydride solvent. The ordinate gives the potential observed between the glass electrode and the mercury–mercurous acetate reference electrode. The generating current was 15.62 mA.

When quantities of base greater than about 0.01 mequiv. were titrated it was observed in the vicinity of the end-point that the potential of the glass electrode did not achieve a steady value for several min after the generation of hydrogen ion had ceased. For such cases it was necessary to generate about 95% of the equivalent amount of hydrogen ion, to wait 5–10 min, and then generate in small increments, with a 2–3 minute pause after each increment, until the potential of the glass elec-

trode was stable. Unless this waiting procedure was followed, the results were consistently 2–5% high. The reasons for the slow approach to equilibrium near the end-point are not clear and a study of this phenomenon is in progress.

### *Solvent system*

The supporting electrolyte used for the coulometric generation consisted of a mixture of six parts (by volume) acetic anhydride and one part acetic acid, which was also 0.1 *F* in sodium perchlorate. The large amount of acetic anhydride was advantageous for four different reasons. First, as pointed out by STREULI<sup>7</sup>, many substances display stronger basic properties in an acetic anhydride solvent than in acetic acid. Our observations confirmed this for potassium hydrogen phthalate and sodium acetate. Sharper end-points were obtained in the mixed solvent than in acetic acid alone.

A second advantage of the acetic anhydride stems from its dielectric constant which is over twice as great as that of glacial acetic acid. As a result, the sodium perchlorate is more ionized in the mixed solvent and the conductivity of the 0.1 *F* sodium perchlorate solution is about ten times greater than is a saturated (*ca.* 0.6 *F*) solution of sodium perchlorate in acetic acid. This greater conductivity makes it much simpler to maintain a constant generating current with the mixed solvent solution than when the supporting electrolyte is prepared from pure acetic acid.

It was found that the addition of sodium perchlorate to acetic acid solutions of weak bases caused such a large depression in the potential inflection at the end-point that the precision with which a titration could be carried out was seriously reduced. In the mixed acetic acid–acetic anhydride solvent, however, this undesirable effect of the sodium perchlorate was much less pronounced and precise titrations resulted.

Finally, the presence of even small amounts of water in a glacial acetic acid solvent causes the end-point in an acidimetric titration to be much more poorly defined. The presence of the large excess of acetic anhydride in the mixed solvent ensures that the solvent remains virtually completely anhydrous.

### *Blank titrations and corrections*

The 0.1 *F* sodium perchlorate supporting electrolyte solution used for the generation of hydrogen ion was observed to contain small amounts of basic impurities (*ca.*  $2 \cdot 10^{-5}$  mequivs. per ml). These impurities were corrected for by pretitrating the supporting electrolyte to a potential inflection, adding the aliquot of standard base, and continuing the titration to a second potential inflection. The time between the first and second inflections corresponded to the amount of base present. The anhydrous acetic acid which was used to prepare the standard solutions of bases was observed also to contain a very small amount of basic impurity (*ca.*  $10^{-6}$  mequivs. per ml). The size of this impurity was determined by titrating volumetrically a large sample of the acetic acid to an indicator end-point<sup>5</sup>. A correction for this basic impurity in the acetic acid was applied to the titrations of aliquots of the standard solutions of base.

### *Results*

Table I summarizes the results obtained for titrations of standard solutions of potassium hydrogen phthalate and sodium acetate. The sodium acetate was prepared by dissolving sodium carbonate in acetic acid.

The maximum quantity of base that could be titrated was fixed by the fact that with quantities of base greater than about 0.3 mequivs. in 90 ml, the waiting time required for the glass electrode to reach a steady potential became prohibitively long and the titration was no longer practical. The lower limit of the titration is about  $3 \times 10^{-4}$  mequivs. of base because for smaller quantities the potential inflection at the end-point becomes too gradual for precise determinations to be made.

### *Extensions of the titration*

In principle, the method for the coulometric generation of hydrogen ion described here should be applicable to the titration of many of the basic substances which are titratable volumetrically in acetic acid. Exceptions would include those substances, such as easily acylated amines, which react with acetic anhydride to form non-basic products.

TABLE I

<i>Base taken mequivs. <math>\times 10^3</math></i>	<i>Number of titrations</i>	<i>Base found mequivs. <math>\times 10^3</math></i>	<i>% error</i>
Potassium hydrogen phthalate-amalgam electrode			
18.73	7	$18.72 \pm 0.01$	-0.06
37.08	4	$37.08 \pm 0.02$	0.00
92.91	3	$92.88 \pm 0.03$	-0.03
Sodium acetate-amalgam electrode			
0.316	4	$0.312 \pm 0.008$	-1.3
0.627	3	$0.634 \pm 0.005$	+1.1
2.81	4	$2.81 \pm 0.00$	0.00
5.57	3	$5.57 \pm 0.01$	0.00
13.94	3	$13.94 \pm 0.02$	0.00
48.00	2	$48.00 \pm 0.02$	0.00
Sodium acetate-mercury pool electrode			
48.00	3	$47.98 \pm 0.04$	-0.02
94.95	4	$94.91 \pm 0.05$	-0.04
237.9	3	$237.9 \pm 0.1$	0.00
332.9	1	332.6	-0.09

A coulometric titration of fluoride ion has been accomplished with this technique and the details of the titration will be described in a forthcoming publication.

The coulometric generation of hydrogen ion in acetic acid-acetic anhydride mixtures would be more convenient and straightforward if the mercury anode could be replaced by a platinum generator anode. The oxidation of acetic acid at a platinum anode would provide a means for generating hydrogen ions with 100% current efficiency if the electrode reaction were reaction (3) or (4). However, it was not found possible to generate hydrogen ion with current efficiencies greater than about 95% by oxidizing the acetic acid-acetic anhydride mixture at a platinum anode. The side reactions which are responsible for the decreased current efficiencies have yet to be

established. The possibility that hydrogen ion could be generated by oxidizing species such as hydroquinone, formic acid, or acetaldehyde at a platinum anode is presently under investigation. Preliminary experiments have shown that the oxidation of hydrobenzoquinone to benzoquinone and hydrogen ion does proceed with 100% titration efficiency at a platinum electrode in the acetic acid-acetic anhydride solvent system.

#### ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (W.B.M.)

#### SUMMARY

A technique for the coulometric generation of hydrogen ions in an acetic acid-acetic anhydride-sodium perchlorate electrolyte by anodically oxidizing a mercury electrode is described. Accurate coulometric titrations of sodium acetate and potassium hydrogen phthalate have been carried out. The technique should be applicable to many of the basic substances which can be titrated volumetrically in acetic acid.

#### RÉSUMÉ

Les auteurs proposent une technique de titrages acidimétriques par coulométrie dans l'acide acétique anhydre. On a pu effectuer ainsi des dosages précis d'acétate de sodium et de biphthalate de potassium. Applications possibles également pour de nombreux autres composés basiques.

#### ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur coulometrischen Erzeugung von Wasserstoffionen in einem Essigsäure-Essigsäureanhydrid-Natriumperchlorat Elektrolyt und deren Anwendung zur coulometrischen Titration von Natriumacetat und Kaliumhydrogenphthalat. Weitere Anwendungsmöglichkeiten werden erwähnt.

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## GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING UP TO 218° IN A LOW-TEMPERATURE COAL TAR\*

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### INTRODUCTION

Detailed analysis of low-temperature coal tar will lead to clearer understanding of the chemical structure of the tar and thus help both in the study of the mechanism of carbonization and the development of uses for the tar.

As a part of a broad low-temperature coal tar characterization program, this paper presents the results of analysis of the aromatic hydrocarbons, boiling up to 218°, present in the neutral oil portion of a low-temperature bituminous coal tar.

Previously only 28 aromatic hydrocarbons boiling between 80–218° were found in low-temperature bituminous coal tars by means of older analytical techniques<sup>1-4</sup>. In 1956 GRANT AND VAUGHAN<sup>5</sup> described the gas-liquid chromatographic analysis of aromatic hydrocarbons in coal tar naphthas and identified benzofuran, an unspecified methyl styrene, and six other aromatic hydrocarbons boiling up to 178° in two low-temperature coal tars; of these, only the methyl styrene was not previously reported.

In the present work, gas-liquid chromatography and other modern techniques were used for analysis; 52 aromatic hydrocarbons boiling up to 218° were found in a low-temperature bituminous coal tar, and their quantities were determined.

A correlation was established between relative retention and boiling points for some alkyl benzenes, whereby identification of several other aromatic hydrocarbons was made possible.

Besides indans, benzofurans, and indenenes the aromatic hydrocarbons identified are methylated, ethylated, or propylated benzenes. Up to the present, no butyl benzenes have been found in this particular tar. Of the 52 compounds found, 27 had not been previously reported to be present in a low-temperature bituminous coal tar.

Another phase of the work concerning analysis of higher boiling aromatic hydrocarbons, such as biphenyls and alkyl naphthalenes, several of which have already been identified in this laboratory, is being completed and the results will be reported later.

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\* Presented at the Symposium on Tars, Pitches and Asphalts at the American Chemical Society meeting in Boston, Mass., April, 1959.

## EXPERIMENTAL WORK AND RESULTS

*I. Preparation of aromatic hydrocarbon concentrates from the coal tar for gas-liquid chromatography*

*Isolation of neutral oil from tar distillate.* The tar used in this work was made from a West Virginia, Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at about 480–510°. The raw tar was deashed, dehydrated, and topped to about 175° at the plant. The tar distillate had been obtained in this laboratory under very mild temperature conditions calculated to be equivalent to about 350–360° at atmospheric pressure with a yield of 20.8 weight-percent of the tar in the main distillate and less than 1% collected in a dry ice trap.

About 3 l (2660 g) of the main distillate were extracted according to the method of FISHER AND EISNER<sup>6</sup> to remove tar acids and tar bases. The neutral oil thus obtained was washed three times with an equal volume of water. After it had been passed through a filter made of three layers of filter paper on a funnel, the oil was dried in a desiccator over anhydrous calcium chloride for a week. About 2400 ml (2180 g) of dry neutral oil, corresponding to 82% by weight of the distillate and 16.9% by weight of the tar, was obtained.

*Fractional distillation of the neutral oil.* A 698-g charge of the neutral oil was fractionally distilled in a PODBIELNIAK Hyper-Cal high-temperature automatic distillation apparatus. The column was 8 mm by 36 inches and was packed with Heli-Grid packing. The end-point chosen for this distillation was a pot temperature of 200° to avoid any significant thermal alterations. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

*Separation of the neutral oil fractions into chemical types by displacement chromatography.* The silica gel adsorption method based on displacement chromatographic techniques, which have been applied to petroleum distillates<sup>7</sup> and shale-oil naphthas<sup>8</sup>, was adapted for separating the aromatic hydrocarbons from saturates and unsaturates.

The column chosen for this work consisted of an upper section 22 cm long and 10 mm I.D. and a lower section 138 cm long and 3 mm I.D. The entire column was jacketed to provide water for cooling or heating as required.

The column was packed with Davison Grade 950 silica gel, 60–200 mesh, which had been freshly activated at 160° for 4 h just before packing. About 26 g of silica gel were needed for the column. A fresh batch of silica gel was used for each run.

The sample was charged to the column, using about 3 p.s.i.g. oxygen-free nitrogen pressure. The desorbents selected were two different alcohols, the choice being made on the basis of the relative kinematic viscosities of the sample and the alcohol. An alcohol could be selected for each fraction so that its viscosity would be somewhat greater than that of the fraction. The alcohols were also chosen for desorbents on the basis of miscibility with the samples, and ease of removal from the last portions of the charge desorbed. After the sample was charged to the column, it was followed immediately by the desorbent with about 10 p.s.i.g. nitrogen pressure.

The operating temperature chosen for each sample depended on the melting points

TABLE I

## FRACTIONATION OF NEUTRAL OILS IN PODBIELNIAK STILL

Charge: 16.92 wt.-% of the tar			
698 g			
Distillate: 360 g = 51.6%			
Residue: 338 g = 48.4%			
Fraction No.	Head temperature °C, 50 mm	Estimated b.p. °C, 760 mm	Weight g
1	77.5-87.5	163-180	4.43
2	87.5-94.0		
3	94.0-101.4	180-190	3.94
4	101.4-104.3	190-192	4.53
5	104.3-109.0	192-198	9.81
6	109.0-114.5	198-202	9.61
7	114.5-118.3	202-210	25.95
8	118.3-121.8		
9	121.8-124.2	210-213	5.29
10	124.2-126.5	213-220	17.88
11	126.5-130.9		
12	130.9-132.9	220-225	14.80
13	132.9-134.2		
14	134.2-137.3	225-230	12.78
15	137.3-139.9	230-233	18.36
16	139.9-141.5	233-235	17.11
17	141.5-141.9	235-236	14.13
18	141.9-145.9	236-240	11.54
19	145.9-149.4	240-243	18.46
20	149.4-151.6	243-246	18.84
21	151.6-153.5	246-248	19.22
22	153.5-155.0	248-250	20.57
23	155.0	250	18.55
24	155.0-155.8	250-251	6.34
25	155.8-157.8	251-253	18.46
26	157.8-158.0	253-253	18.46
27	158.0-159.9	253-254	18.07
28	159.9-162.0	254-256	21.34
29	162.0-163.0	256-260	11.53
Total			360.00

of the expected components in the fraction. If some of them were crystalline at room temperature, a temperature near the melting points of the components was used.

Fractions were obtained with an automatic fraction collector which counted drops photoelectrically and maintained the fractions in an atmosphere of oxygen-free nitrogen.

Usually only the very last fraction was contaminated by the desorbent. The desorbent was removed by extracting with 80 to 90% glycerin, and the glycerin was then removed with several water washings. The alcohol- and glycerin-free sample was dried overnight over anhydrous calcium chloride in a partly evacuated desiccator. The refractive index was obtained on each fraction, and by comparing these values with literature values for pure hydrocarbons in the boiling range of the charge it was readily estimated where the paraffins and naphthenes, olefins, aromatics, and neutral oxygen, nitrogen and sulfur compounds were located among the fractions. With this technique, no sharp borderlines could be expected between two adjacent types. However, it was found that overlapping occurred only in the very first and the very last fractions of any one type.

Since this paper covers the first six distillate fractions boiling from 163°–202°, the data on displacement chromatography for only these fractions are given in Table II. About 17 drops per displacement fraction were collected, except for the last one, which consisted of about 50 drops.

## II. Analysis of aromatic hydrocarbons by gas-liquid chromatography

*Apparatus and operating conditions.* A Perkin-Elmer model 154C Vapor Fractometer was used. The response range of the recorder was 0–11 mV, and the speed of the chart was 3.75 in./h. The peak areas produced by components of the sample on the chromatogram were measured with a planimeter.

The column for this work was made from a 15-ft.  $\times$  1/4-in. O.D. copper tubing filled with approximately 50 g of packing made of 25% Apiezon L grease on 30–60 mesh fire brick. After being packed, the column was coiled to fit into the column chamber of the Fractometer.

The temperature chosen for the analysis was 150°, approximately 10° below the lowest boiling fraction and 50° below the highest boiling fraction. Samples were injected with 10 or 50  $\mu$ l-syringes. The carrier gas was helium, admitted to the column at a pressure of 12 lb./in.<sup>2</sup>, corresponding to a flow rate of 95 ml/min. The outlet pressure was atmospheric. The voltage for the bridge of the thermoconductivity detector was 8 V, and the most sensitive range was used. Throughout the work the temperature stayed within  $\pm 0.1^\circ$ , and the carrier gas pressure and the voltage of the bridge stayed constant.

The efficiency of the column under these conditions, referring to *n*-propylbenzene and to 1,2,3,5-tetramethylbenzene, was 3520 and 3885 theoretical plates, respectively, calculated by using the equation<sup>9</sup>, No. of theoretical plates =  $16(x/y)^2$ , where  $y$  = length of peak baseline (as defined), and  $x$  = length from start of run to middle of baseline section.

*Sample collecting system for gas-liquid chromatography.* The original fraction collecting system for the Perkin-Elmer instrument has a short length of 1/8-in. stainless-steel tubing leading from the detector cell to an external syringe needle adapter that has a three-way syringe valve. This is intended for attaching a short needle, which can be inserted through a rubber serum bottle cap at the bottom of a solvent-filled tube for washing effluent gas in order to collect fractions. However, this type of collector was found to be unsatisfactory in most instances.

A new fraction-collecting system was devised, which would take advantage of the existing needle adapter. This involved heating the stainless-steel tubing electrically to prevent the fractions from condensing, and using 6-in, 18-gauge syringe needles cooled with powdered dry ice as fraction collectors. Holders for dry ice powder were made from 110-mm lengths of 18-mm O.D. glass tubing, which were wrapped with aluminum foil and asbestos string, and plugged at one end with 12 mm thick cork stoppers, each having a small hole in the center for entry of the needles. To collect the material producing a chromatogram peak, one of the needles was fastened to the upright needle adapter and one of the dry ice jackets was slipped down over the needle, the insulating cork plug resting on the hot needle hub. The jacket was carefully packed with dry ice powder and the three-way valve turned to admit effluent gas to the needle. After a sample was collected, the needle was removed, a Teflon plug

TABLE II  
DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No.	1 + 2	3	4	5	6
Weight of charge, g	1.77	3.15	3.60	7.40	7.7c
Desorbent	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Butyl alcohol
Saturates + some olefins:					
Number of fractions	5	3	4	7	5
Refractive index range, $n_D^{20}$	1.3930-1.3941	1.4381-1.4832	1.4252-1.4471	1.4328-1.4695	1.4400-1.4683
Total weight, g	0.74	0.61	1.20	2.11	1.93
Aromatics + some olefins + some O, S compounds:					
Number of fractions	4	5	5	9	12
Refractive index range, $n_D^{20}$	1.3941-1.5007	1.4832-1.5310	1.4911-1.5397	1.4912-1.5545	1.4895-1.5601
Total weight, g	0.70	2.29	2.17	4.32	5.21
N, S, and O compounds retained on column, g	0.33	0.25	0.23	0.97	0.56
Weight of aromatic hydrocarbons identified by GLC, g	0.57	1.95	1.66	4.30	4.81

inserted at the hub end, and a little polyethylene tube slipped over the needle end and placed in a Dewar flask containing dry ice. The infrared spectrum of the sample was subsequently obtained in a 0.05 or 0.1-mm microcell for identification of the components. The infrared microcell was filled by inserting the needle tip into the cell and introducing a fraction of a drop of carbon disulfide into the needle hub. However, in some instances it was necessary to wash out the needle with about  $\frac{1}{2}$  ml carbon disulfide, collecting the solution in a 1-ml beaker and carefully evaporating off solvent with a gentle stream of nitrogen until about 1 drop of solution remained. This was then placed in the microcell by capillary action, using the capillary tubing of the cell. Good infrared spectra were obtained with about 1 mg hydrocarbon, in particular, there was no contamination from compounds producing adjacent peaks.

*General approach for identification.* The retention times of 42 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained for preliminary identification of the unknowns. The relative retentions at 150° and 200° of the 42 aromatics, referred to *n*-propylbenzene, are shown in Table III. These relative retention values can be considered to be either relative retention times or relative retention volumes.

The aromatic fractions obtained by displacement chromatography of the first six distillate fractions were examined individually by gas-liquid chromatography under the same conditions for the known compounds. To confirm the identification the material producing each peak was collected for infrared spectrophotometric analysis. Three methods were used to identify the aromatic hydrocarbons present in the fractions.

The first method of identification consisted of a combination of conventional gas-liquid chromatography and infrared spectrophotometry. The retention times of unknown peaks were compared with those of known compounds for preliminary identification. The material producing each peak was then collected in a microcell for an infrared spectrum, as previously described. The confirmation of identity was then made by comparing this spectrum with that of the known compound.

Retention times could not, of course, be obtained for those compounds for which authentic specimens were not available. A second method of identification was used for these compounds which involved the correlation curves of relative retentions and boiling points; these are shown in Fig. 2 and explained in detail in a later section. Boiling points of the unknowns producing peaks were obtained from their relative retentions by these correlation curves and were used as a preliminary means of identification. Since literature infrared spectra of a number of compounds were available, conformation could be made in these instances.

For a third group of compounds, neither the retention times nor the infrared spectra of authentic specimens were available. However, from the correlation curves and the relative retentions of the unknown peaks, tentative identification could be made through the boiling points. Also, by correlating infrared absorption bands and molecular structures, these tentative identities could be substantiated further.

To illustrate the first and second methods of identification, the chromatogram of a typical fraction is shown in Fig. 1, and the boiling points of the components producing the peaks (as obtained from the correlation curves) are presented in Table IV. Excellent agreement is shown between literature and predicted boiling points. The

TABLE III

LITERATURE BOILING POINTS, RELATIVE RETENTIONS AND CALIBRATION FACTORS ( $f_c$ ) OF SOME AROMATIC HYDROCARBONS

Compound	Literature b.p. °C 760 mm <sup>a</sup>	Relative <sup>b</sup> retention (150°)	$f_c$ (150°) <sup>a</sup>	Relative <sup>b</sup> retention (200°)
Methylbenzene	110.626	0.36	1.02	0.48
Ethylbenzene	136.186	0.62	0.95	0.64
1,4-Dimethylbenzene	138.351	0.67	0.98	0.70
1,3-Dimethylbenzene	139.104	0.68	1.00	0.71
1,2-Dimethylbenzene	144.411	0.77	1.01	0.82
Isopropylbenzene	152.392	0.83	1.02	0.86
<i>n</i> -Propylbenzene	159.217	1.00	1.00	1.00
1-Methyl-3-ethylbenzene	161.305	1.06	1.01	—
1-Methyl-4-ethylbenzene	161.989	1.09	1.08	1.06
1-Methyl-2-ethylbenzene	165.153	1.21	1.06	1.17
1,3,5-Trimethylbenzene	164.716	1.19	1.08	1.13
1,2,4-Trimethylbenzene	169.351	1.38	1.03	1.29
1,2,3-Trimethylbenzene	176.084	1.67	1.04	1.52
Indan	177.82	1.82	1.65	1.69
Isobutylbenzene	172.759	1.33	1.07	1.26
<i>sec.</i> -Butylbenzene	173.305	1.34	1.08	1.27
<i>n</i> -Butylbenzene	183.27	1.77	1.04	1.56
1-Methyl-3-isopropylbenzene	175.14	1.39	1.07	1.27
1-Methyl-4-isopropylbenzene	177.10	1.48	1.04	1.35
1-Methyl-2-isopropylbenzene	178.15	1.58	0.94	1.42
1-Methyl-3- <i>n</i> -propylbenzene	181.80	1.71	1.03	1.51
1-Methyl-4- <i>n</i> -propylbenzene	183.30	1.76	1.03	1.58
1-Methyl-2- <i>n</i> -propylbenzene	184.80	1.90	1.07	1.67
1,3-Diethylbenzene	181.102	1.62	1.00	1.45
1,2-Diethylbenzene	183.423	1.81	1.06	1.60
1,4-Diethylbenzene	183.752	1.79	1.03	1.58
1,3-Dimethyl-5-ethylbenzene	183.75	1.82	1.09	1.59
1,2,4,5-Tetramethylbenzene	196.80	2.77	0.93	2.28
1,2,3,5-Tetramethylbenzene	198.00	2.87	1.06	2.33
Indene	182.44	1.92	1.10	1.80
1-Methylindene	199	2.22	1.20	1.98
2-Methylindene	208	3.48	1.15	2.96
1-Methyl-3,5-diethylbenzene	200.70	2.68	1.11	2.14
1,2,3,4-Tetrahydronaphthalene	207.57	3.84	2.05	3.13
1,4-Diisopropylbenzene	208.9	3.26	—	2.49
1,2-Diisopropylbenzene	209	3.06	—	2.51
Benzofuran	171.38	1.35	1.15	1.33
Naphthalene	217.96	4.68	1.14	3.51
1,3,5-Triethylbenzene	216.2	3.87	—	1.13
Pentamethylbenzene	231.8	7.08	—	4.87
$\alpha$ -Methylstyrene	165.5	1.22	1.11	1.14
$\beta$ -Methylstyrene ( <i>trans</i> )	178.26	1.64	1.09	1.47

TABLE III (continued)

Compound	Literature b.p. °C 760 mm <sup>a</sup>	Relative <sup>b</sup> retention (150°)	f <sub>c</sub> (150°) <sup>c</sup>	Relative <sup>b</sup> retention (200°)
1,4-Dimethyl-2-ethylbenzene	186.91	2.04 <sup>d</sup>	—	1.73 <sup>d</sup>
1,2-Dimethyl-4-ethylbenzene	189.75	2.17 <sup>d</sup>	—	1.89 <sup>d</sup>
1-Methylindan	190.6	2.30 <sup>d</sup>	—	1.99 <sup>d</sup>
1,2-Dimethyl-3-ethylbenzene	193.91	2.50 <sup>d</sup>	—	2.06 <sup>d</sup>
5-Methylindan	202.0	3.25 <sup>d</sup>	—	2.67 <sup>d</sup>
1-Methyl-3,4-diethylbenzene	203.6	3.00 <sup>d</sup>	—	—
4-Methylindan	205.5	3.46 <sup>d</sup>	—	2.81 <sup>d</sup>
1,2,3,4-Tetramethylbenzene	205.04	3.48 <sup>d</sup>	—	2.81 <sup>d</sup>
3-Methylindene	205	3.50 <sup>d</sup>	—	2.82 <sup>d</sup>

<sup>a</sup> All values, except for benzofuran, from API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa. Benzofuran b.p. from J. N. BRESTON and A. W. GAUGER, *Proc. Am. Gas Assoc.*, 28 (1946) 492.  
<sup>b</sup> Dead volume corrected.  
<sup>c</sup> Defined in eq. 1.  
<sup>d</sup> The relative retentions of these compounds were determined from tar components identified by I.R.

peak numbers in Fig. 1 are explained in Table IV. This chromatogram was produced by a 10-μl sample of an aromatic cut of  $n_d^{20} = 1.5074$ , from distillate fraction 5 in a boiling range of 192–198°. Peak 1 is produced by *n*-propylbenzene, the internal standard, added to the cut for quantitative estimation of the components. The components producing peaks 2, 3, 4, 9, 10 and 11 were identified by comparing the retention times with those of known compounds. The components producing peaks 5, 6, 7, 8, 12, 13 and 14 were identified through their boiling points, obtained from their

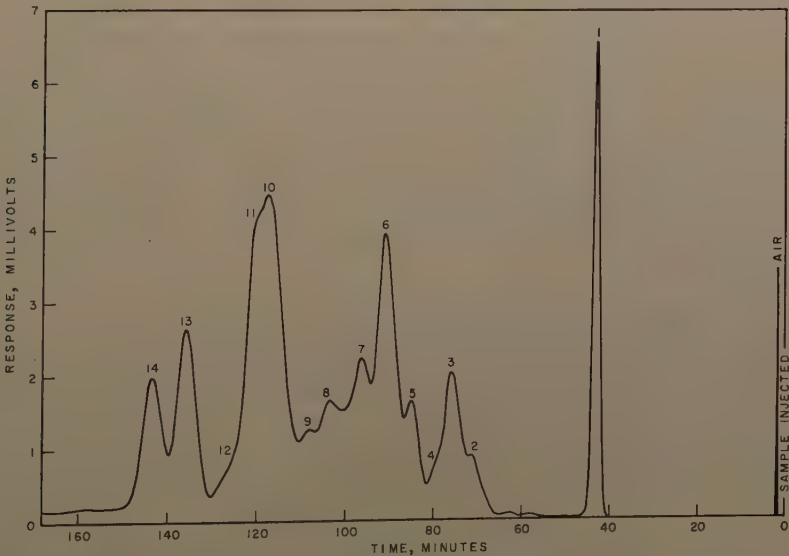


Fig. 1. Chromatogram of an aromatic cut obtained from distillate fraction 5.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF AN AROMATIC CUT FROM DISTILLATE FRACTION 5

Peak No.	Relative retention	Compound identified	Relative retention of known compound	Boiling point °C	
				from literature	from correlation curve
1	1	<i>n</i> -Propylbenzene (added standard)	1	159.2	159.2
2	1.69	1-Methyl-3- <i>n</i> -propylbenzene	1.71	181.8	181.3
3	1.82	1,3-Dimethyl-5-ethylbenzene	1.82	183.8	183.7
4	1.89	1-Methyl-2- <i>n</i> -propylbenzene	1.90	184.8	184.9
5	2.02	1,4-Dimethyl-2-ethylbenzene	*	186.9	186.1
6	2.16	1,2-Dimethyl-4-ethylbenzene	*	189.8	189.3
7	2.29	1-Methylindan	*	190.6	191.3
8	2.46	1,2-Dimethyl-3-ethylbenzene	*	193.9	193.5
9	2.65	1-Methyl-3,5-diethylbenzene	2.68	200.7	200.1
10	2.79	1,2,4,5-Tetramethylbenzene	2.77	196.8	197.6
11	2.86	1,2,3,5-Tetramethylbenzene	2.87	198.0	198.4
12	3.00	1-Methyl-3,4-diethylbenzene	*	203.6	204.1
13	3.25	5-Methylindan	*	202.0	202.6
14	3.45	4-Methylindan	*	205.5	204.5

\* Authentic specimens not available for determination of retention times.

relative retention and the correlation curves. To confirm the identities, a 25  $\mu$ l-sample was used to produce enough material for each major peak for infrared spectrophotometric analysis. However, the minor ones, such as 4, 8, 9 and 12, were better confirmed by the infrared spectra of the material producing the corresponding peaks in the chromatogram of an adjacent aromatic cut.

Table V illustrates the third method of identification. It is to be noted that the identities of three compounds were substantiated further by considering the infrared absorption bands and probable molecular structures according to the correlations of BELLAMY<sup>10</sup>. Two compounds were present in the last two distillate fractions (Nos. 5 and 6) in such small quantities that no satisfactory infrared spectra were obtained. Infrared spectra were obtained, however, for the components producing all the significant chromatogram peaks. It was observed that only a few weak absorption bands were unaccounted for by the compounds identified. The relative intensities of these bands were such that these unknown components could have been present in only trace amounts.

#### Quantitative estimation of aromatic hydrocarbons

The internal standard method was adapted for quantitative analysis of the samples, *n*-propylbenzene being selected as the standard. KEULEMANS, KWANTES AND RIJNDERS<sup>11</sup> have demonstrated the use of an average calibration factor,  $f_c$ , defined as follows, for calibrating areas and percentages for a component, and an internal standard for obtaining precise quantitative analysis of light hydrocarbons:

$$f_c = A_s W_c / A_c W_s \quad (1)$$

where  $A_s$  and  $A_c$  are the areas for the internal standard and component in the

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TABLE V  
DATA FOR TENTATIVE IDENTIFICATION OF FIVE ALKYL BENZENES

Name of compound	Literature b.p., °C 760 mm	Relative retention of the unknown peak	B.p., °C obtained from the correlation curve	Infrared spectral-structural correlations
1,4-Dimethyl-2-isopropylbenzene	196.2	2.38	196.6	—
1,3-Dimethyl-2- <i>n</i> -propylbenzene	207.6	3.35	207.7	—
1,4-Dimethyl-2- <i>n</i> -propylbenzene	203.6	3.04	204.6	12.23 $\mu$ (S): 2H out-of-plane deformation vibration. 11.39 $\mu$ (M): 1H out-of-plane deformation vibration. 9.12 $\mu$ (W): 9.47 $\mu$ (W); 9.90 $\mu$ (MW) suggest 1,2,4-substitution of benzene ring. Probable structure: 1,2,4-trialkylbenzene.
1-Methyl-2,4-diethylbenzene	205.0	3.10	205.2	12.40 $\mu$ (S): 2H out-of-plane deformation vibration. 11.30 $\mu$ (M): 1H out-of-plane deformation vibration. 9.60 $\mu$ (W): 9.70 $\mu$ (W); and 8.65 $\mu$ (W) suggest 1,2,4-substitution of benzene ring. Probable structure: 1,2,4-trialkylbenzene.
1,2-Dimethyl-3- <i>n</i> -propylbenzene	210.7	3.64	210.5	12.81 $\mu$ (S) and 14.32 $\mu$ (M): 3H out-of-plane deformation vibration. 8.67 $\mu$ (W): 1,2,3-substitution of benzene ring. Probable structure: 1,2,3-trialkylbenzene.

mixture, and  $W_c$  and  $W_s$  are the weight-percentages of the component and the standard.

In order to investigate the deviation of the average calibration factors of aromatic hydrocarbons from the actual values in a certain range of concentrations, eight pure compounds (namely, 1-methyl-3-ethylbenzene, 1,3,5-trimethylbenzene, indan, 1,3-diethylbenzene, indene, 1,3-dimethyl-5-ethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,3,4-tetrahydronaphthalene) were used. Three solutions of each compound in different concentrations, about 15, 30, and 60% by weight, were prepared in *n*-propylbenzene. Using these 24 solutions, the  $f_c$  values were then calculated from the weight-percentages and the peak areas produced by the components in their chromatograms. It was found that the average  $f_c$  in the concentration range of 15–60% by weight had a maximum deviation of only about  $\pm 3\%$  from the actual values, and the best results were obtained at concentration ranges of 30–60%. This is considered accurate enough for estimating the amounts of aromatic components present in such a complex mixture as coal tar. The  $f_c$  values for the rest of the aromatic hydrocarbons were determined only once at 150° at a concentration of 40–50%. These  $f_c$  values are shown in Table III and were used to determine the weight percentages of all aromatic hydrocarbons in the fractions. For those compounds which were not available in this laboratory but found to be present in the sample, the  $f_c$  value of its isomers or of a structurally similar compound was used.

Two synthetic blends were analyzed by using these  $f_c$  values, and the results are shown in Table VI.

For analyzing the components in the sample, a certain amount of the internal standard, *n*-propylbenzene, roughly 15% by weight, was added to each of the sample fractions so that the peak area of the standard approximately equaled that of the major peaks. A new chromatogram of each fraction, after the addition of the standard, was then made. The percentage of each component was then calculated by using

TABLE VI  
ANALYSIS OF SYNTHETIC BLENDS

Blend	Component	Relative retention	Wt. % present	Wt. % found		
				Run 1	Run 2	Run 3
A	Isopropylbenzene	0.82	10.28	10.31	10.47	10.77
	<i>n</i> -Propylbenzene	1.00	11.67	—	—	—
	1,3,5-Trimethylbenzene	1.29	12.93	12.91	12.82	12.61
	1-Methyl-2-isopropylbenzene	1.56	12.62	12.14	12.16	12.54
	Indan	1.82	19.07	18.08	18.60	18.34
	Indene	1.92	14.71	15.03	15.05	14.67
	1,2,3,5-Tetramethylbenzene	2.88	18.72	19.16	19.19	18.66
	Total		100.00	99.30	99.96	99.26
B	<i>n</i> -Propylbenzene	1.00	14.64	—	—	—
	sec.-Butylbenzene	1.35	18.14	17.62	17.42	—
	1-Methyl-4-isopropylbenzene	1.48	15.23	14.91	14.97	—
	1-Methyl-3- <i>n</i> -propylbenzene	1.72	17.07	16.97	17.09	—
	1,3-Dimethyl-5-ethylbenzene	1.84	21.37	21.28	21.54	—
	1-Methylindene	2.23	13.64	13.54	13.76	—
	Total		100.00	98.96	99.42	—

equation (1). In the few instances of unresolved components, conventional quantitative infrared analysis was used.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table VII. The values of wt. % in neutral oil for the highest boiling components are not entered, since it is expected that more of these compounds will be found in distillate fractions 7 and 8.

## DISCUSSION

*Correlation between relative retention and boiling points of alkylbenzenes having an equal number of carbon atoms*

DESTY AND WHYMAN<sup>12</sup> plotted the boiling points of a large number of low-boiling paraffinic hydrocarbons and a few aromatic hydrocarbons against the logarithm of their relative retention volumes for two different stationary phases, resulting in two almost straight lines for each of the solvents. These plots indicate the selectivity of the two stationary phases for these two different types of solutes and offer help in choosing a suitable solvent for the separation of these two general types. However, no relationship between the relative retentions and boiling points of alkylbenzenes

TABLE VII

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING UP TO 200° IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt. g	Wt. % in neutral oil <sup>a</sup>
Methylbenzene <sup>b</sup>	1, 2	Rel. retention	—	1 <sup>c</sup>	Trace
Ethylbenzene <sup>b</sup>	1, 2	Rel. retention	—	2 <sup>c</sup>	Trace
1,3- and 1,4-Dimethylbenzene <sup>b</sup>	1, 2	Rel. retention	—	9 <sup>c</sup>	Trace
1,2-Dimethylbenzene <sup>b</sup>	1, 2	Rel. retention	—	20 <sup>c</sup>	Trace
Isopropylbenzene <sup>b</sup>	1, 2	Rel. retention	—	79 <sup>c</sup>	Trace
n-Propylbenzene <sup>b</sup>	1, 2	Rel. retention, I.R.	d	250 <sup>c</sup>	0.002
1-Methyl-3-ethylbenzene <sup>b</sup>	1, 2	Rel. retention, I.R.	e	0.010	0.001
1-Methyl-4-ethylbenzene <sup>b</sup>	1, 2	Rel. retention, I.R.	e	0.0098	0.001
1-Methyl-2-ethylbenzene <sup>b</sup>	1, 2	Rel. retention, I.R.	e	0.0075	0.001
1,2,3-Trimethylbenzene <sup>b</sup>	1, 2	Rel. retention, I.R.	e	0.3105	0.045
1,2,4-Trimethylbenzene <sup>b</sup>	1, 2, 3	Rel. retention, I.R.	e	0.2695	0.039
1,3,5-Trimethylbenzene <sup>b</sup>	1, 2, 3	Rel. retention, I.R.	e	0.1184	0.017
1-Methyl-4-isopropylbenzene	1, 2, 3, 4	Rel. retention, I.R.	d	0.0596	0.009
1-Methyl-3-isopropylbenzene	1, 2, 3, 4	Rel. retention, I.R.	d	0.0511	0.007
1-Methyl-2-isopropylbenzene	3	Rel. retention, I.R.	d	0.0164	0.002
1,2-Diethylbenzene	3, 4	Rel. retention, I.R.	e	0.0857	0.012
1,3-Diethylbenzene	3, 4	Rel. retention, I.R.	e	0.1009	0.015
1,4-Diethylbenzene <sup>b</sup>	4	Rel. retention	—	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene <sup>b</sup>	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	e	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	e	0.7698	0.110
1,3-Dimethyl-5-ethylbenzene <sup>b</sup>	3, 4, 5, 6	Rel. retention, I.R.	d	1.0872	0.156
1,2-Dimethyl-3-ethylbenzene <sup>b</sup>	4, 5, 6	Rel. retention-b.p. correlation, I.R.	e	0.5938	0.085

TABLE VII (continued)

Compounds identified	Fractions	Method of identification	Source of I.R. spectrum	Total wt. g	Wt. % in neutral oil <sup>a</sup>
1-Methyl-3- <i>n</i> -propylbenzene	3, 4, 5	Rel. retention, I.R.	d	0.3180	0.046
1-Methyl-2- <i>n</i> -propylbenzene	5	Rel. retention, I.R.	d	0.0753	0.011
1,2,4,5-Tetramethylbenzene <sup>b</sup>	4, 5, 6	Rel. retention, I.R.	d	1.1066	0.159
1,2,3,5-Tetramethylbenzene	5, 6	Rel. retention, I.R.	d	1.7690	0.253
1,2,3,4-Tetramethylbenzene <sup>b</sup>	6	Rel. retention-b.p. correlation, I.R.	e	0.8852	—
Indene <sup>b</sup>	1, 2, 3, 4	Rel. retention, I.R.	e	0.2331	0.033
3-Methylindene	5, 6	I.R.	e	0.5378	—
Indan <sup>b</sup>	1, 2, 3	Rel. retention, I.R.	d	0.3945	0.057
1-Methylindan	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	f	1.1265	0.161
5-Methylindan	5, 6	Rel. retention-b.p. correlation, I.R.	f	1.4976	—
4-Methylindan <sup>b</sup>	5, 6	Rel. retention-b.p. correlation, I.R.	f	1.4988	—
1,3-Dimethyl-2- <i>n</i> -propylbenzene	5	Rel. retention-b.p. correlation	—	0.0173	0.003
1,2-Dimethyl-3- <i>n</i> -propylbenzene	5, 6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.1008	—
1,4-Dimethyl-2- <i>n</i> -propylbenzene	5, 6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.4124	—
1,4-Dimethyl-2-isopropylbenzene <sup>b</sup>	5	Rel. retention-b.p. correlation	—	0.1151	0.017
1-Methyl-3,5-diethylbenzene	5, 6	Rel. retention, I.R.	d	0.2393	0.034
1-Methyl-2,4-diethylbenzene	6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.6505	—
Styrene	1, 2	I.R.	g	0.0332	0.005
4-Methylstyrene	1, 2	I.R.	h	0.0225	0.003
$\beta$ -Methylstyrene ( <i>trans</i> )	1, 2	Rel. retention, I.R.	d	0.1396	0.020
3-Phenyl-1-butene	1, 2	I.R.	g	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	5,6	Rel. retention, I.R.	d	0.3171	—
Naphthalene <sup>b</sup>	6	I.R.	d	0.0886	—
Benzofuran <sup>b</sup>	1, 2	Rel. retention, I.R.	d	0.0991	0.014
5-Methylbenzofuran	3	I.R.	g	0.1432	0.021
6-Methylbenzofuran	3, 4	I.R.	g		
2-Methylbenzofuran	4	I.R.	g	0.1681	0.024
3-Methylbenzofuran	4	I.R.	g		
7-Methylbenzofuran	3, 4	I.R.	g	0.0785	0.011

<sup>a</sup> Total neutral oil distilling up to about 360°, representing 16.92 wt. % of the total tar.

<sup>b</sup> Previously identified by others<sup>1-5</sup>.

<sup>c</sup> Ratio to methylbenzene.

<sup>d</sup> This laboratory.

<sup>e</sup> American Petroleum Institute, Research Project 44, infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

<sup>f</sup> JACOB ENTEL, CLARENCE H. ROUF, AND H. C. HOWARD, *Anal. Chem.*, 25 (1953) 1303.

<sup>g</sup> SAMUEL P. SADTLER & SON, Inc., Philadelphia, Pa.

<sup>h</sup> Courtesy of W. F. HAMNER, Monsanto Chemical Co., Texas City, Texas.

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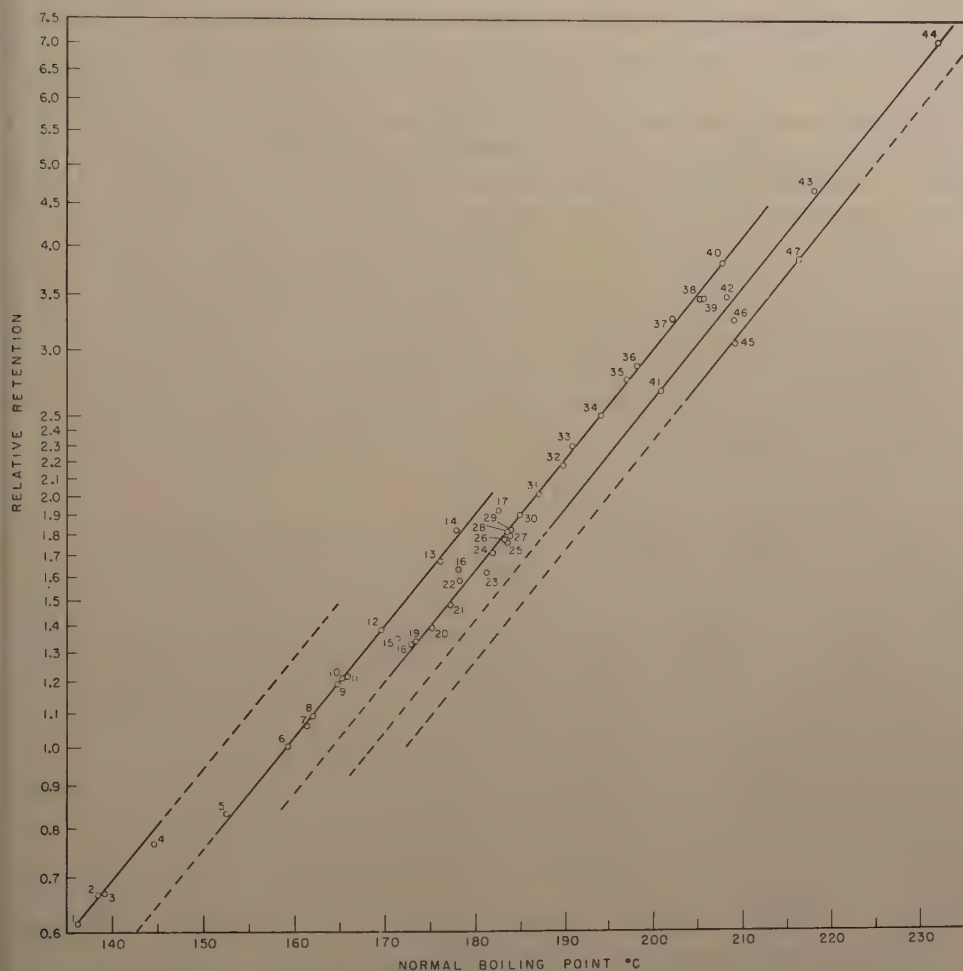


Fig. 2. Correlation between relative retentions and boiling points of some aromatic hydrocarbons at 150° on Apiezon L grease.

1. Ethylbenzene, 2. 1,4-Dimethylbenzene, 3. 1,3-Dimethylbenzene, 4. 1,2-Dimethylbenzene, 5. Isopropylbenzene, 6. *n*-Propylbenzene, 7. 1-Methyl-3-ethylbenzene, 8. 1-Methyl-4-ethylbenzene, 9. 1,3,5-Trimethylbenzene, 10. 1-Methyl-2-ethylbenzene, 11.  $\alpha$ -Methylstyrene, 12. 1,2,4-Trimethylbenzene, 13. 1,2,3-Trimethylbenzene, 14. Indan, 15. Benzofuran, 16.  $\beta$ -Methylstyrene, 17. Indene, 18. Isobutylbenzene, 19. *sec*-Butylbenzene, 20. 1-Methyl-3-isopropylbenzene, 21. 1-Methyl-4-isopropylbenzene, 22. 1-Methyl-2-isopropylbenzene, 23. 1,3-Diethylbenzene, 24. 1-Methyl-3-*n*-propylbenzene, 25. 1-Methyl-4-*n*-propylbenzene, 26. *n*-Butylbenzene, 27. 1,4-Diethylbenzene, 28. 1,2-Diethylbenzene, 29. 1,3-Dimethyl-5-ethylbenzene, 30. 1-Methyl-2-*n*-propylbenzene, 31. 1,4-Dimethyl-2-ethylbenzene, 32. 1,2-Dimethyl-4-ethylbenzene, 33. 1-Methylindan, 34. 1,2-Dimethyl-3-ethylbenzene, 35. 1,2,4,5-Tetramethylbenzene, 36. 1,2,3,5-Tetramethylbenzene, 37. 5-Methylindan, 38. 4-Methylindan, 39. 1,2,3,4-Tetramethylbenzene, 40. 1,2,3,4-Tetrahydronaphthalene, 41. 1,3-Diethyl-5-methylbenzene, 42. 2-Methylindene, 43. Naphthalene, 44. Pentamethylbenzene, 45. 1,2-Diisopropylbenzene, 46. 1,4-Diisopropylbenzene, 47. 1,3,5-Triethylbenzene.

having an equal number of carbon atoms in the alkyl group has ever been expressed for the purpose of identifying this type of hydrocarbon. When the logarithms of relative retention for alkylbenzenes with an equal number of carbon atoms in the alkyl group were plotted against their boiling points, a straight line resulted. Fig. 2 shows five such lines corresponding to alkylbenzenes having 2, 3, 4, 5, and 6 carbon atoms in the alkyl groups. It is interesting to see that these lines are parallel to each other. There is a similar correlation at 200°.

Indans and tetralin, which have a benzene nucleus and a fused saturated ring, fall closely on the correlation curves for alkylbenzenes with the corresponding number of carbon atoms in the alkyl group and therefore are included in these series. Indenes, styrenes, and naphthalene which have a double bond in the "side chain", however, do not follow the corresponding curves and appear to have a different pattern. From the limited data obtained at present, no correlation can be found for these types.

These correlation curves can be expressed by the following empirical equation:

$$\text{Log } V_R = mT_B - c \quad (2)$$

where  $V_R$  = relative retention of an alkyl benzene,  $T_B$  = normal boiling point of the compound, °C,  $m$  = slope,  $c$  =  $Y$  — intercept at any temperature; 0° arbitrarily selected.

The slope for the set of five alkylbenzene series at 150° on a stationary phase of Apiezon L grease is 0.0134, and their intercepts on the vertical axis at 0° are 2.0294, 2.1242, 2.1937, 2.2498, and 2.2952 for alkylbenzenes with 2, 3, 4, 5, and 6 carbon atoms in the alkyl group. The values of the intercept  $c$  are, of course, a measure of the separation of the five parallel lines from each other.

The intercept  $c$  in eqn. 2 can be correlated with the number of carbon atoms in the alkyl group,  $N_C$ , as shown in Fig. 3. This can be expressed as follows:

$$\text{Log } N_C = a \log c - b \quad (3)$$

where  $N_C$  = number of carbon atoms in the alkyl group,  $a$  = slope,  $b$  = intercept.

For the curve shown in Fig. 3,  $a = 8.78$  and  $b = 2.431$ .

From eqn. 3, it is possible to generate a family of relative retention-boiling-point curves when only one is known.

The relationship between relative retentions and boiling points of alkylbenzenes was found to be very useful for characterization. For example, peak 6 in the chromatogram shown in Fig. 1 has a relative retention of 2.16. By checking the curves in Fig. 2, it was readily determined that the boiling point of this unknown in a distillate fraction boiling at about 192–198° should be 189.3° if it is an alkylbenzene having four carbons in the alkyl group or 193.5° if it has an alkyl group of five carbon atoms. 1,2-Dimethyl-4-ethylbenzene boils at 189.79° and 1-methyl-3-isobutyl- and 1-methyl-3-*sec*-butylbenzene both boil at 194°. The infrared spectrum of the collected material producing this peak agreed very well with that of 1,2-dimethyl-4-ethylbenzene.

#### *Calibration factor ( $f_c$ ) and type of aromatic hydrocarbon*

An examination of the calibration factor ( $f_c$ ) data in Table III disclosed that the molecular structure of the compounds plays an important role in determining the value of this factor, while within each type the variation in value is relatively small.

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Referring to Table III, for all alkylbenzenes the values are 0.93–1.10, with an average of nearly 1.0; for indenenes, styrenes, and naphthalene, 1.15, 1.1, and 1.14; and for indan and tetralin, 1.65 and 2.05. Considering the benzene nucleus as a common structural center for all compounds, the alkylbenzenes are obviously in one group; styrenes, indenenes, and naphthalene, which all have unsaturation in the other part of the molecule, form another group; indan and tetralin, with the non-benzene part saturated and cyclic, are different from the other two groups. The difference between

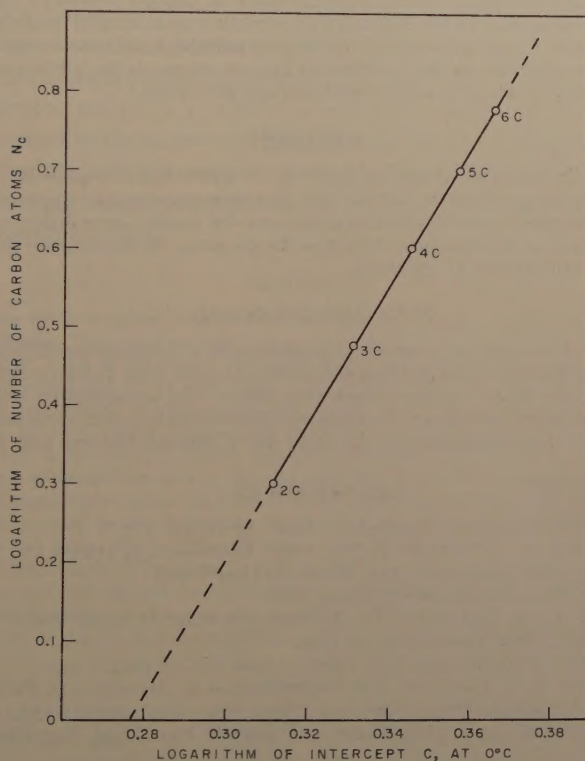


Fig. 3. Correlation between number of carbon atoms in the alkyl group,  $N_c$ , and intercept  $C$  at  $0^\circ$ .

indan and tetralin is probably due to the number of carbon atoms in the saturated cyclic part of the molecule. It is interesting to note that benzofuran, having an unsaturated part in addition to the benzene nucleus, has a value of 1.15, quite similar to that of the second group although it contains an oxygen atom.

Based on this observation about the  $f_c$  values and structures,  $f_c$  values for some hydrocarbons that were not available in this laboratory were assumed to be equal to those of either their isomers or of structurally similar compounds. Thus,  $f_c$ , 1.09, for 1,3-dimethyl-5-ethylbenzene was used for estimation of all dimethylethyl benzenes; 1.11 for 1-methyl-3,5-diethylbenzene for all methyldiethyl benzenes; 1.65 of indan for all methyl indans; 1.15 of benzofuran for all methyl benzofurans, and 1.00, an average value for 1,2,4,5- and 1,2,3,5-tetramethylbenzene, for 1,2,3,4-tetramethylbenzene.

## ACKNOWLEDGEMENTS

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## SUMMARY

52 Aromatic hydrocarbons boiling up to  $218^{\circ}$  were identified in a low-temperature bituminous coal tar by means of gas-liquid chromatography and infrared spectrophotometry, 27 of these for the first time. Quantitative determinations were made on 43 compounds boiling up to  $200^{\circ}$ . It was shown that alkylbenzenes with equal numbers of carbon atoms in their alkyl groups exhibit a linear relationship between log relative retention and normal boiling point, and that the  $C_8$ ,  $C_9$ ,  $C_{10}$ ,  $C_{11}$ , and  $C_{12}$  alkylbenzenes lie on five parallel lines whose separation from each other is related to the logarithm of the number of carbon atoms in the alkyl group. Examples of the accuracy and utility of these novel correlations are presented.

## RÉSUMÉ

Cinquante-deux hydrocarbures aromatiques (P.E.  $< 218^{\circ}$ ) dont 27 pour la première fois, ont pu être identifiés dans un goudron de houille, par chromatographie gaz-liquide et spectrophotométrie infra-rouge. Quarante-trois de ces composés ont été dosés. Cette étude a permis d'obtenir d'utiles renseignements sur la structure chimique du goudron, le mécanisme de la carbonisation et pour de nouvelles utilisations du goudron.

## ZUSAMMENFASSUNG

In Tief-Temperatur Bitumenteer konnten 52 aromatische Kohlenwasserstoffe mit Siedepunkten bis zu  $218^{\circ}$  mit Hilfe der gas-flüssig Phasenchromatographie und Infrarot-Spektrophotometrie identifiziert werden, wovon 27 Verbindungen zum ersten Mal aufgefunden wurden. 43 Verbindungen wurden quantitativ bestimmt. Es konnten Gesetzmässigkeiten zwischen dem chromatographischen Verhalten (Retentionswerte), der Zahl der Kohlenstoffatome und den Siedepunkten aufgedeckt werden.

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## Short Communication

### Determination of traces of nickel in uranium

A rapid method was required for the determination of microgram amounts of nickel in uranium. Dimethylglyoxime in ammoniacal solution has long been used for the determination of small amounts of nickel<sup>1,2</sup> but none of the reported methods<sup>2-4</sup> is satisfactory for the direct determination of nickel in uranium. The method proposed here uses an elevated pH ( $11.5 \pm 0.5$ )<sup>5,6</sup> in order to obtain a stable colour. This high pH could be attained without precipitation of uranium, thorium, iron, etc., by using ammonium carbonate and ammonium citrate as the complexing agent. The limit of determination is  $5 \mu\text{g}$  nickel per gram of  $\text{U}_3\text{O}_8$ ; this can be extended to 1 p.p.m. by using a 5-cm absorption cell.

#### PROCEDURE

Two 1-g samples were weighed into 100-ml beakers, dissolved in nitric acid and the solutions evaporated to dryness. The residue was taken up with 1 ml of 1:1 sulphuric acid and diluted to 20 ml with water. 2 ml of saturated bromine water were added and the solution set aside for 5 min, after which ammonia (1:1) was added dropwise to destroy the excess of bromine and to form a permanent precipitate of ammonium diuranate. 10 ml of 25% (w/v) ammonium carbonate solution and 2 ml of 25% (w/v) ammonium citrate solution were then added and the solution cooled to about  $20^\circ$ . 8 ml of 25% (w/v) sodium hydroxide solution were added dropwise with stirring and the pH adjusted to  $11.5 \pm 0.5$  by addition of a few drops of sodium hydroxide solution. 2 ml of dimethylglyoxime reagent (1% in alcohol) were added to one of the beakers, the other solution serving as the reference blank. The solutions were made up to 50 ml in volumetric flasks and set aside for 30 min for full colour development. After this time, the colour was stable for at least 24 h. The absorbancy of the solution was measured on a spectrophotometer at  $530 \text{ m}\mu$  and the nickel concentration determined by reference to a standard curve prepared by taking between 5 and  $100 \mu\text{g}$  of nickel in the presence of 1 g of  $\text{U}_3\text{O}_8$  and following the same procedure.  $50 \mu\text{g}$  Ni in a 1-cm cell at  $530 \text{ m}\mu$  showed an optical density of 0.15.

TABLE I

Interfering metal	Amount added $\mu\text{g}$	Ni added $\mu\text{g}$	Ni found $\mu\text{g}$
Copper(II)	50	10.0	10.0
	100	10.0	10.0
	50	30.0	30.0
	100	30.0	29.5
Cobalt(II)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.5
Chromium(III)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.0

Copper(II), cobalt(II), and chromium(III) are the only interfering metals but their colours with dimethylglyoxime are much weaker than the nickel colour<sup>1</sup>; the

effects of these elements are shown in Table I. No interference occurs if the amounts in the sample aliquot are 50  $\mu\text{g}$  or less; the interference is slight if the amount of the interfering metal is 100  $\mu\text{g}$ .

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#### REVUES DE LIVRE

Source material for radiochemistry – Nuclear science series – Report number 27 – Subcommittee on radiochemistry – Committee on nuclear science – Publication number 654, National Academy of Science, National Research Council, Washington D.C., mars 1959.

Il est fort difficile d'obtenir des renseignements précis et complets sur la bibliographie concernant la radiochimie. Le sous-Comité en radiochimie a comblé cette lacune. Dans son No. de mars 1959, il donne une liste de 60 références (primary documents) avec, en quelques lignes, l'objet de celles-ci et, initiative heureuse, l'adresse exacte permettant de se procurer l'ouvrage désiré.

D. MONNIER (Genève)

*Papierchromatographie*, Heft 2, et *Ionenaustauscher* par Dr. HERBERT DAECKE. Otto Salle Verlag, Frankfurt, Hamburg, 1959, 43 p. DM. 3.80.

Ces opuscles font partie de la collection *Schriftenreihe zur Chemie*. L'auteur y expose, en quelques pages, les principes essentiels, les applications et le mode opératoire de la séparation chromatographique sur papier et des échangeurs d'ions. Présentation claire, très simplifiée qui convient particulièrement bien à tous ceux qui désirent s'initier à ces remarquables techniques de séparation, parmi les plus importantes de l'analyse chimique moderne. Une bibliographie sommaire, mais soigneusement choisie donne le titre des principaux traités généraux parus dans le domaine de la chromatographie et des échangeurs d'ions ainsi qu'un certain nombre de monographies et d'ouvrages plus particulièrement axés sur le mode opératoire.

D. MONNIER (Genève)